# THE JOURNAL

OF THE

# AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVII MARCH 1952 No. 3


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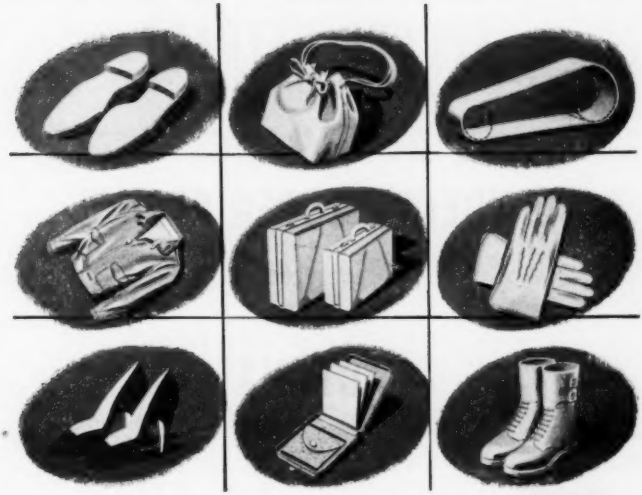

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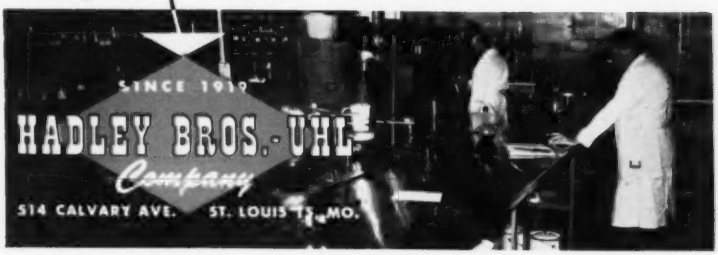

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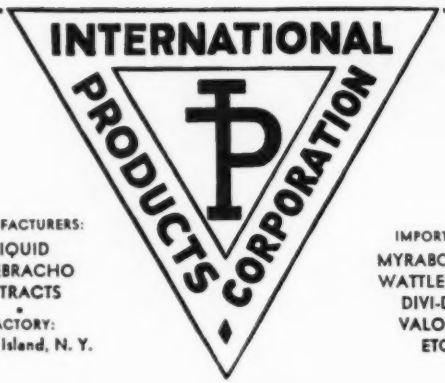


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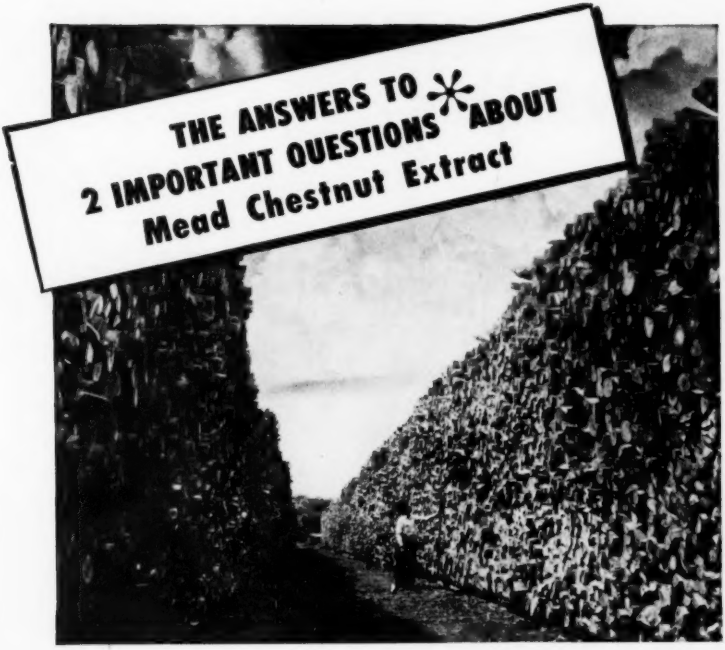


This is only a portion of the many stockpiles of chestnut logs that insure a continuous supply of Chestnut Extract.

**1. Is the supply of Mead Chestnut Extract adequate?**

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**A.** Chestnut tanned leathers do not oxidize, darken on exposure to light, or develop an uneven color on aging, as do leathers tanned with many other materials, vegetable or synthetic.

**B.** Since the tanning system demands acid, the use of chestnut, with its plumping acidity, saves you money.

**C.** Mead Chestnut Extract eliminates up to 28% of leachhouse losses.

**D.** There are no hidden costs. When you use Mead Chestnut Extract, no time- and money-consuming preparation is required.

Ask about Mead Cold Soluble Chestnut Extract for retanned leathers. And—for more pounds of plumper leather—standardize on Mead Chestnut Extract.

## IT'S A FACT!

Mead Chestnut Extract will produce more pounds of plump leather per unit of tannin than any other tanning material.

| Vegetable Tannin | Tan Yard Yield (*white weight basis*) |
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| Chestnut Wood Extract | 67% |
| Tanning Material A | 61% |
| Tanning Material B | 63% |

Calculate your tanning material costs on a leather basis as well as on a tan unit basis. Mead Chestnut Extract, producing four to six pounds more leather, means positive savings.

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CHESTNUT
EXTRACT

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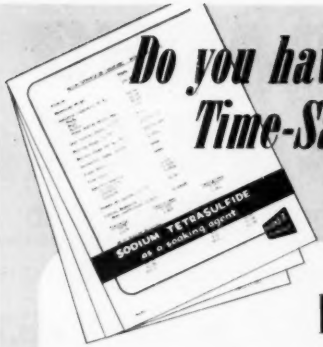


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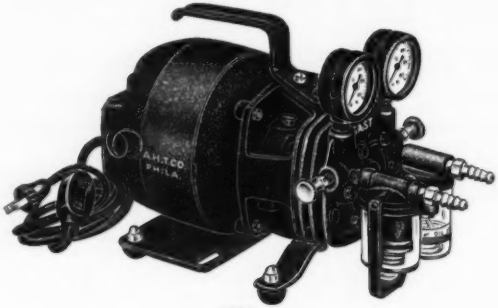


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JOURNAL OF THE
# AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVII MARCH 1952 No. 3

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## SECRETARY'S NOTICE

Due to a change in employment, Mr. Fred Thayer has withdrawn his name as President-Elect Candidate. The Nominating Committee has proposed as a replacement, Mr. John W. Harnly, on the ballot.

Any 15 active members can nominate candidates. Their petition and a statement of the willingness of the nominee to serve if elected must be in the Secretary's hands by April 1st. No member shall sign more than one petition for each office to be filled.

## CANDIDATES FOR THE 1952 ELECTION

For President-Elect:

FREDERICK D. THAYER, JR.
EDWIN S. FLINN

For Members of Council:

F. LESLIE COLLINS
W. ROBERT LOTZ
CHESTER A. ROSS
ROBERT G. WELDON

The above slate of candidates has been prepared by the Nominating Committee.

WILLIAM R. COX
CLINTON E. RETZSCH
C. A. BLAIR, *Chairman.*

Members Note:

Article V – 2 Nominations – (c)

Additional candidates may be nominated by petitions, signed by 15 or more active members. Such petitions shall reach the Secretary not later than April 1st, and shall contain a statement of the willingness of the nominee to serve if elected. No member shall sign more than one petition for each office to be filled.

---

# A Method for Predicting Dye Penetration on Leather

W. K. SCHWEITZER, JR. †* and R. M. LOLLAR

*Department of Basic Science in Tanning Research*
*Foundation Tanners' Council of America*
*University of Cincinnati*
*Cincinnati, Ohio*

Numerous studies have been made in the past of the various factors influencing the penetration of dyes on leather; however, a literature search has failed to reveal any reliable means of predicting this penetration. Attempts have been made to correlate the penetration of dyes with their molecular structure, but this is generally unsatisfactory because of the great variation in any given dye caused by differences in the manufacturing process and by the presense of diluent salts in commercial dyes. This investigation has indicated that these differences have a much greater influence on the penetrating ability of the dyes on leather than is generally realized.

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*The Hilton-Davis Fellow 1949–1951.

In the past, most investigations of dye penetration on leather have followed the penetration of the dye microscopically on leather that has been dyed either commercially or in the laboratory. However, when the great number of dyes presently available is considered, it is immediately apparent that such work is extremely time-consuming and expensive. Also, these results are not necessarily transferable to commercial practice under different dyeing conditions and with all types of stock. It is desirable that an accurate, rapid, and inexpensive method for predicting the penetration of dyes on leather be presented. Tanners have developed methods, usually retained as trade secrets, to use the capillary of the dyes on filter paper as an estimate of their penetration into leather. Although it has been generally recognized that penetration, adsorption, and capillarity of dyes on textiles are inter-related [8], the literature does not indicate that this also is true for leather. Therefore, the following work has been done to determine if such a relationship does exist.

## Experimental

To study the relationship between penetration of the dyes on leather and the capillarity of these dyes, it was first necessary to establish a reproducible means of dyeing the leather and, secondly, a means of determining the depth of dye penetration. It was initially assumed that leather samples that exhaust the dye bath equally under the same dyeing conditions were identically dyed. Thus the extent of exhaustion of the dye bath, which is easily determined spectrophotometrically, was the principal criterion of reproducibility of the dyeing.

*A. Development of a Standard Dyeing Procedure*—As a starting point, the methods used in the experimental work of Nestler and Royer [5] and by the Society of Dyers and Colourists [2] and those recommended for commercial practices were combined and a tentative procedure established. Then, as optimum operating conditions were determined, the procedure was modified. The dyes were chosen from lists of those recommended by Wilson [10], Orthmann [16] and various dyestuff manufacturers. Since acid dyes are the type in most general use in the leather industry, many of the dyes were of this type, although some basic and direct dyes were also studied. In order to check the differences between manufacturers, each dye was obtained from at least four sources, and in all, about 90 dyes were used.

The type of skin and the processing that it received before dyeing has some effect on the penetration of the dyestuffs. For this study a commercially chrome tanned calfskin "in the blue" (4.7 per cent chrome oxide on the hide substance basis) was used because of its relatively uniform epidermal area and the fact that it is a type of stock and tannage in large scale production. Because some basic dyes were used, it was necessary to mordant the leather with a vegetable extract to permit dyeing; all studies were therefore made on

vegetable-bottomed pieces. The possibility of using sheep skin skivers was also investigated. These pieces proved to be too thin under the conditions used, and only dyes with slight penetrating power could be compared.

One dye (Orange G, C. I. 27) was selected for standardization of the dyeing procedure. This choice was based on the assumption that Orange G is a typical acid dye and that it has good penetrating power; also it is a dye that is commonly used in the leather industry. The minimum transmittance wave length of this dye was determined with the Beckman DU Spectrophotometer and its extinction coefficient was calculated. It was found that changes in pH and salt concentration within the ranges normally encountered in leather dyeing did not appreciably change these values. Then using the methods of Monego and von Bergen [4] the concentration of this dye in solution may be determined.

The general dyeing method developed to determine the different variables was as follows:

1. Chrome tanned calfskin is cut into specimens 2 x 6 inches with the long axis parallel to the backbone. Each specimen is marked to record its location. The specimens, wrapped in aluminum foil, are held in a deep freeze unit (–10°F.) until used.
2. The specimens are brought to a uniform condition of neutralization [11] before use by soaking in water for one hour, followed by neutralization in five times their weight by acetate buffer (0.2 *N*, pH 4.0) for exactly 15 minutes.
3. The specimens are placed in groups of two for the dyeing with the ends of each specimen stapled together, grain out, to prevent sticking. To each pair, three grams of a 25 per cent solution of five per cent bisulfited quebracho and 50 ml. of water are added. The samples are then run for 30 minutes in a launderometer at 120°F. At the end of the run, the liquors are discarded.
4. The samples are washed with 75 ml. of water per set for ten minutes and the water discarded.
5. Seventy-five ml. of one per cent dye are added to each set and they are run for 30 minutes at 120°F. The exhaust liquor is saved for analysis.
6. The samples are then washed for ten minutes with about 50 ml. of water which is then discarded and the samples are tacked to dry.

The weight of the two specimens in each jar is about 25 grams. To reduce the chances of variation, the skins are all shaved to three ounces. This gives a rather constant sample weight. However, the amount of dye is based on area rather than weight, following the suggestion of Lamb [3]. This simplifies the procedure considerably.

Modifications of the dyeing procedure were found to be necessary, as the various steps were studied, to obtain reproducible exhaustion values. The largest source of variation was found to be in the selection of sample areas. The most reproducible results were obtained on samples cut from the bend area of the skin. Therefore, all subsequent work was done only on samples that came from an area extending 10 inches on either side of the backbone (excluding the backbone itself) and 30 inches forward from the root of the tail.

Neutralization was found to have a very great effect on the depth of penetration of the dyes. The 15 minute neutralization in acetate buffer was found to give the best results. Other modifications had very little beneficial effect on the exhaustion reproducibility.

*B. Microscopic Techniques*—Sections of samples dyed by the above procedure were cut with the freezing microtome, placed in water and mounted with glycerine jelly. A minimum of three cross-sections of each dyeing was made. Penetration was determined at least three times on each cross-section by measurement using a calibrated ocular in the microscope.

*C. Filter Paper Capillary Measurement*—Sheets of Schleicher & Schuell Company filter paper No. 602 were soaked in a 10 per cent solution of quebracho (25 per cent quebracho, 5 per cent bisulfited) in water for five minutes and dried overnight. They were then cut into strips 4″ x ½″ for use. The dye solution was prepared by dissolving four grams of commercial dye in 376 ml. of water at the boil and then adding 20 ml. of 0.2 *N* acetate buffer at pH 4.0. Formic acid was used to help solubilize the basic dyes. The solutions were cooled and allowed to remain at 120°F. for a minimum of one hour to attain equilibrium before they were used.

The dye solution was placed into six 300 ml. tall form beakers in 50 ml. aliquots. Then two strips of the mordanted filter paper were suspended in each beaker, and the beakers were covered. The dye was allowed to rise on the paper for exactly 30 minutes, the paper then being removed. The strips were immediately dried and the capillary rise noted.

In some initial studies unmordanted strips were used with the same procedure. Also, rate studies were made to determine the minimum time needed, the capillarity being measured at various time intervals.

## Discussion of Results

*A. Dyeing Procedure*—The most important variables in the dyeing procedures were the neutralization and selection of sample areas. Reproduction of exhaustion values was found to be possible only within a range. Therefore, every attempt was made to keep this range as small as possible.

Figure I indicates the general areas of the skin from which specimens were cut for dyeing. The specimens themselves were as large as could be conveniently handled in quart jars. Table I lists the exhaustion values obtained

from the various areas. It is obvious that Area I is the least variable and should be best suited. Area II's values overlap those of Area I somewhat, and the range of these values is relatively small. In fact, the range of values from Area I plus those from Area II is about the same as the range for Area II alone. Therefore, it was decided to use specimens from both areas.

FIGURE I

Sampling Areas

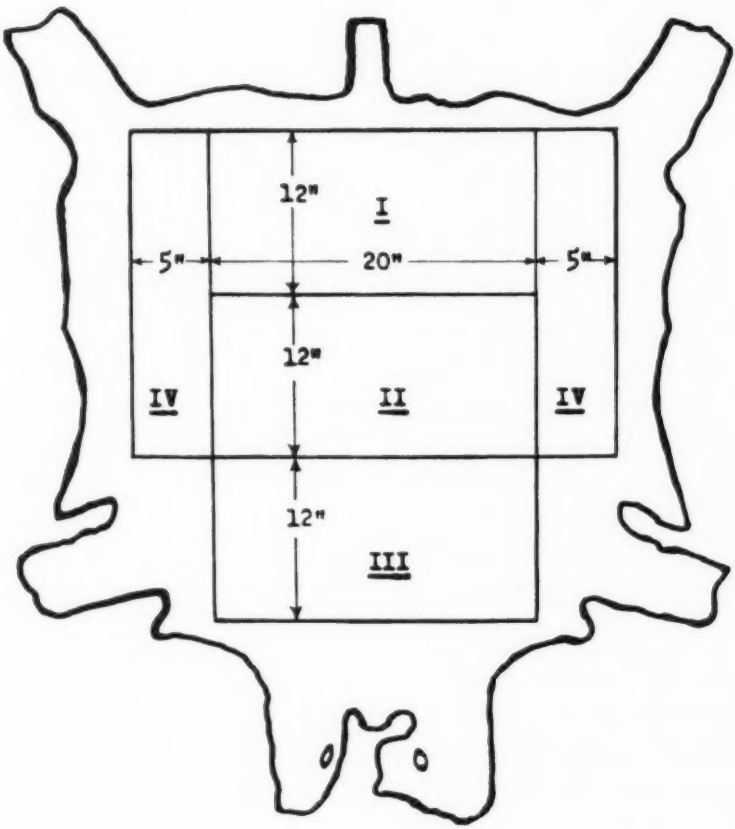


TABLE I

Effect of Leather Area on Exhaustion of Dye Bath
(Data expressed as percentage exhaustion)

| | areas | | | |
|---|---|---|---|---|
| | I | II | III | IV |
| replicas | 69.2 | 70.0 | 72.7 | 71.3 |
| | 69.7 | 71.8 | 73.0 | 74.0 |
| | 68.9 | 70.0 | 73.5 | 71.4 |
| | 68.6 | 70.8 | 70.8 | 72.4 |
| | 71.1 | 70.0 | 72.4 | 74.5 |
| | 70.5 | 72.4 | 73.1 | 74.0 |
| | 69.3 | 70.6 | 74.3 | 72.6 |
| | — | 71.9 | 73.2 | 72.9 |
| | 68.5 | 72.3 | 71.6 | 74.6 |
| | 70.8 | 71.3 | 69.6 | 74.8 |
| | 71.0 | 72.6 | 70.4 | 74.3 |
| | 71.3 | 70.0 | 71.4 | 70.5 |
| | 69.7 | 71.5 | 72.4 | |
| | 70.2 | 69.2 | 70.5 | |
| | | 68.8 | 71.9 | |
| | | 68.7 | 73.0 | |
| High | 71.3 | 72.6 | 74.3 | 74.8 |
| Low | 68.5 | 68.7 | 69.6 | 70.5 |
| Range | 2.8 | 3.9 | 4.7 | 4.3 |
| Average | 69.9 | 70.7 | 72.1 | 74.8 |

Neutralization will not give uniform results unless it is rigidly controlled. It was found that neutralizing for a given time with a buffer was the means of obtaining the most reproducible results. The time of neutralization has some effect on the results also. Table II shows that while a greater exhaustion of the dyebath is obtained in a shorter time, the results cover a wider range. From the data obtained, 15 minutes was chosen as giving the most reproducible values.

TABLE II

Effect of Time on Leather Neutralization on Exhaustion of the Dyebath.
(Data expressed as percentage exhaustion).

| | Time of Neutralization | | |
|---|---|---|---|
| | 5 minutes | 15 minutes | 30 minutes |
| replicas | 75.8 | 70.0 | 72.3 |
| | 71.6 | 71.8 | 71.3 |
| | 74.8 | 70.0 | 72.6 |
| | 73.4 | 70.8 | 70.0 |
| | 70.8 | 70.0 | 71.5 |
| | 71.3 | 72.4 | 69.2 |
| | 73.1 | 70.6 | 68.8 |
| | 71.6 | 71.9 | 68.7 |
| Range | 5.0 | 2.4 | 3.9 |

The other variables were set arbitrarily, conforming as closely as possible to standard commercial practice. From Table III it will be noted that increasing the amount of mordant cuts the exhaustion values, indicating that the affinity of the tanned protein for the dye has been reduced. It has previously been pointed out that reduction of the affinity of the dye for the leather increases penetration. This is also indicated by the loss of intensity of surface coloration when the degree of exhaustion is reduced.

TABLE III

Effect of Quebracho Bottoming on Exhaustion of Dyebath

| Sample | grams Quebracho solution | % Exhaustion |
|---|---|---|
| I | 2 | 72.5 |
| III | 2 | 72.1 |
| V | 2 | 72.7 |
| VII | 2 | 73.0 |
| | AVERAGE: | 72.6 |
| II | 4 | 70.5 |
| IV | 4 | 68.2 |
| VI | 4 | 69.2 |
| VIII | 4 | 69.8 |
| | AVERAGE: | 69.4 |

*B. Capillarity Measurements*—Attemps were made to obtain values of the capillarity of the various dyes on leather sheets, prepared by wet grinding of chrome shavings in a Waring Blender, and then sheeting by a vacuum technique. The dyes, however, did not rise appreciably even over extended periods of time. It had been felt that capillarity values on this type of substrate would be more readily related to the penetration of the dyes on leather, because of the similarity of the leather sheet to the tanned skin. Apparently, the affinity of even the most penetrating dyes for the leather sheets was so great, and their capillary rise so small, that the magnitude of the differences between the individual dyes could not be easily detected. Consequently, this method was abandoned.

Measurements of the capillary rise of the dyes on filter paper that had no quebracho mordant present gave very confusing results. The basic dyes, which do not penetrate well on leather, showed in some cases almost the same capillary values as the penetrating acid dyes, and again only large differences could be detected. However, when the filter paper had been mordanted with quebracho, the affinity of the dyes (especially the basic ones) for the paper was increased to a very marked extent. The acid dyes were generally only slightly affected. Therefore, a means of showing rather small differences in affinity had been obtained. The capillarity measurements are listed in Table IV.

TABLE IV

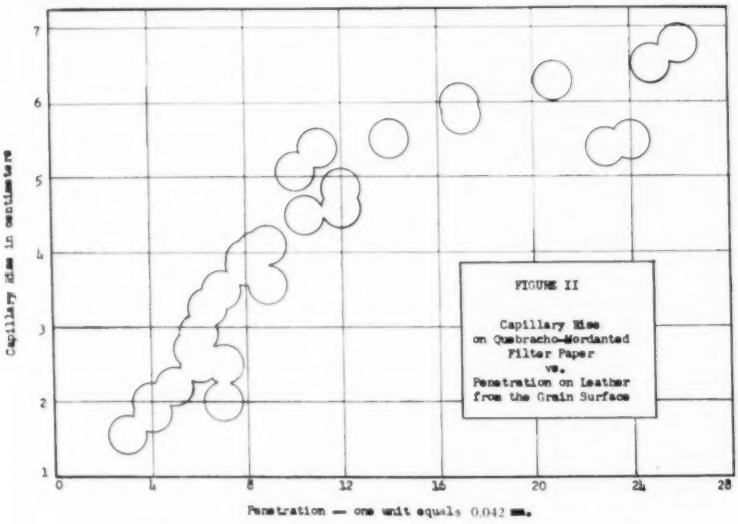
Capillary Rise of Various Dyes on Quebracho-Mordanted Filter Paper in Centimeters

| C. I. | Name of the Dye | Manufacturer | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | A | B | C | D | E | F | G |
| 27 | Orange G | 6.8 | 6.4 | 6.6 | — | 6.4 | — | — |
| 31 | Amido Naphthol Red G | 5.4 | 5.5 | 5.5 | 5.5 | — | — | — |
| 138 | Metanil Yellow | 4.0 | 4.8 | 4.9 | — | 4.7 | — | — |
| 146 | Azo Yellow | — | 3.2 | 4.0 | 2.8 | — | 3.4 | — |
| 151 | Orange II | 5.5 | 6.0 | 6.1 | — | 5.8 | — | — |
| 176 | Fast Red A | — | 5.1 | 6.3 | 5.4 | — | 5.5 | — |
| 234 | Resorcine Brown | — | 3.5 | 4.0 | 2.2 | — | 3.8 | — |
| 235 | Resorcine Dark Brown | 7.4 | 6.7 | — | 7.0 | 6.8 | — | — |
| 246 | Naphthol Blue Black | 4.6 | 5.0 | 4.5 | — | 5.0 | — | — |
| 252 | Brilliant Crocein M | 6.3 | 5.5 | 6.3 | — | 6.0 | — | — |
| 326 | Benzo Fast Scarlet | — | 1.6 | 4.1 | — | 3.6 | 2.2 | — |
| 593 | Diamine Green B | — | 2.2 | 3.4 | 4.9 | 3.4 | — | — |
| 639 | Xylene Light Yellow | 6.7 | 7.1 | 7.1 | — | 6.8 | — | — |
| 640 | Tartrazine | 7.0 | 6.9 | 6.9 | 6.5 | — | — | — |
| 657 | Malachite Green | 1.6 | 1.8 | 2.0 | 2.0 | — | — | — |
| 666 | Guinea Green B | 3.9 | 2.0 | 3.9 | — | 5.0 | — | — |
| 667 | Brilliant Milling Green B | 4.1 | 4.0 | 4.1 | 4.3 | — | — | — |
| 696 | Fast Acid Violet 10 B | 2.6 | 2.1 | 3.0 | — | — | — | 4.6 |
| 698 | Formyl Violet S4B | 4.5 | 3.8 | 2.5 | — | 5.5 | — | — |
| 735 | Naphtholin Green V | 3.6 | 1.6 | 2.0 | 3.6 | — | — | — |
| 737 | Wool Green S | 2.9 | 3.1 | 4.5 | 3.4 | — | — | — |
| 841 | Safranine | 1.8 | 2.2 | 2.8 | 1.6 | — | — | — |
| 922 | Methylene Blue | 2.2 | 1.8 | 2.4 | 2.2 | — | — | — |

Each value in Table IV is the average of a minimum of 12 determinations, and, in almost every case, none of the values varied more than 0.2 centimeter from the average. Statistical analysis showed that in most cases a difference between manufacturers of the same dye of about 0.2 centimeter was mathematically significant at the five per cent level. It was later determined that differences of about 0.1 cm. in capillarity were equivalent to approximately 0.05 mm. in the penetration of the dye on leather under the operating conditions used.

*D. Correlation of Capillarity and Penetration on Leather*—In Figure II the capillarity of 34 of the dyes on quebracho mordanted filter paper is plotted against their penetration on leather, dyed under conditions mentioned previously, and determined microscopically (listed in Table V). The size of the points gives some indication of their degree of uncertainty. It will be noted that the curve falls off as it approaches higher values and the highest value indicates complete penetration. This is to be expected in view of the fact that the capillary rise must necessarily be limited by the height to which the

solvent front will rise for the given time. The correlation coefficient [1] for this linear plot was calculated and found to be 0.89. The shape of the curve suggests that it could be rectified to a better approximation of a straight line by plotting the capillarity against the logarithm of the penetration. This was done and the correlation coefficient in this case is 0.95. The tabular minimum value for the coefficient at the 0.1 per cent level is 0.53. Hence, we may say with a high degree of certainty that the variables are related.




The extremely high degree of significance of the correlation of capillarity on cellulose and penetration on leather is interpreted to mean that differences in the penetrating powers of the dyes are primarily dependent upon the properties of the dyes themselves, and are relatively independent of the substrate. This view is also supported by the work of Pelet-Jolivet and Jess [8] although their studies were conducted on filter paper and textile fabrics. From this we may conclude that, although other factors may change the depth of penetration of the dyes, they will not change the relative order of penetration. Also, the types of leather will not affect the relative order of pentration of the dyes, although it may affect the depth of penetration. This conclusion may logically be applied only to any one class of dyes (i. e. acidic or basic) since factors that increase the affinity of one class decrease the affinity of the other; and as mentioned previously, affinity influences the penetration.

TABLE V

Dyestuff Penetration of Leather from the Grain Surface

| C. I. | Dye Name | Manufacturer | Capillarity Value (cm.) | Penetration Micrometer Units* |
|---|---|---|---|---|
| 326 | Benzo Fast Scarlet | B | 1.6 | 3 |
| 657 | Malachite Green | A | 1.6 | 3 |
| 841 | Safranine | A | 1.8 | 4 |
| 735 | Naphtholin Green V | C | 2.0 | 4 |
| 922 | Methylene Blue | A | 2.2 | 5 |
| 146 | Azo Yellow | D | 2.8 | 5.5 |
| 696 | Fast Acid Violet 10 B | A | 2.6 | 6 |
| 737 | Wool Green S | A | 2.9 | 6 |
| 146 | Azo Yellow | B | 3.2 | 6.5 |
| 666 | Guinea Green B | B | 2.0 | 7 |
| 698 | Formyl Violet S4B | C | 2.5 | 7 |
| 234 | Resorcine Brown | B | 3.5 | 7 |
| 326 | Benzo Fast Scarlet | E | 3.6 | 7 |
| 698 | Formyl Violet S4B | B | 3.8 | 8 |
| 666 | Guinea Green B | A | 3.9 | 8 |
| 138 | Metanil Yellow | A | 4.0 | 8.5 |
| 146 | Azo Yellow | C | 4.0 | 8.5 |
| 735 | Naphtholin Green V | C | 3.6 | 9 |
| 667 | Brilliant Milling Green B | C | 4.1 | 9 |
| 176 | Fast Red A | B | 5.1 | 10 |
| 698 | Formyl Violet S4B | A | 4.5 | 10.5 |
| 176 | Fast Red A | D | 5.4 | 11 |
| 246 | Naphthol Blue Black | A | 4.6 | 12 |
| 138 | Metanil Yellow | B | 4.8 | 12 |
| 151 | Orange II | A | 5.5 | 14 |
| 252 | Brilliant Crocein M | B | 5.5 | 14 |
| 151 | Orange II | E | 5.8 | 17 |
| 252 | Brilliant Crocein M | E | 6.0 | 17 |
| 252 | Brilliant Crocein M | C | 6.3 | 21 |
| 252 | Brilliant Crocein M | A | 6.3 | 21 |
| 31 | Amido Naphthol Red G | A | 5.4 | 23 |
| 31 | Amido Naphthol Red G | C | 5.5 | 24 |
| 640 | Tartrazine | D | 6.5 | 25 |
| 27 | Orange G | A | 6.8 | 26 |

*One unit is equivalent to 0.042 millimeters

In order to determine whether an interaction between the dyes and quebracho influenced the correlation, the capillarity of several dyes was also determined on filter paper mordanted with other extracts. Chestnut extract and a commercial preparation containing an unknown amount of quebracho were used as mordants. Table VI shows the capillary rise of the various dyes on filter paper treated with each of these extracts. In each case, the correlation between penetration of the dyes on quebracho-bottomed leather and the

capillary rise on the various filter papers showed a significant semi-log relationship at the 0.1 per cent level. Also, in no case did the relative order of capillary rise change. Therefore, the conclusions outlined above are validated.

TABLE VI

Comparison of the Capillary Rise in Centimeters of Several Dyes on Filter Paper Treated with Various Mordants

| C. I. | Name | Filter Paper Treated with | | |
|---|---|---|---|---|
| | | Bisulfited Quebracho | Commercial Extract | Chestnut Extract |
| 841 | Safranine | 1.8 | 1.2 | 2.0 |
| 737 | Wool Green S | 2.9 | 1.9 | 3.9 |
| 666 | Guinea Green B | 3.9 | 2.2 | 4.9 |
| 698 | Formyl Violet S4B | 4.5 | 3.1 | 5.2 |
| 151 | Orange II | 5.5 | 3.4 | 5.5 |
| 252 | Brilliant Crocein M | 6.3 | 4.1 | 6.0 |
| 27 | Orange G | 6.8 | 5.3 | 6.8 |

The relationship between capillarity and penetration may be used as a means of evaluating dyestuffs for combinations where dyes of equal penetrating powers are desired. The limitations of the data presented, however, should also be recognized. It is unlikely that differences of less than 0.5 cm. on the mordanted filter paper (roughly equivalent to 0.2 mm. in penetration on leather) could be detected on the finished leather, especially if the shades were similar. Also, possible interactions between the dyes in a combination may exhibit some effects.

Examination of Table V will also disclose that the penetration of any given dye may also vary with the manufacturer. These differences in many cases are quite large and cannot be ignored. The dye, Brilliant Crocein M (C. I. 252), for example, can be obtained with various penetrating properties depending upon the source. It is also possible that the penetrating powers of a dye may vary between batches from the same manufacturer and hence, to obtain uniformity in the finished product, a constant check should be made of all shipments received.

## Summary

1. A standard laboratory method for the dyeing of chrome tanned calf skin has been developed, and it has been shown that the exhaustion on the dyebath may be determined spectrophotometrically. The bend area has been shown to yield the most uniform exhaustion results.

2. A simple, rapid method for predicting the penetration properties of acid, basic, and direct dyes on leather has been developed.

3. The correlation of capillarity of dyes on filter paper and the penetration of these same dyes on leather has been demonstrated. The relative penetra-

tion of dyes on leather has been shown to be a function of the dye rather than the substrate.

4. It has been shown that the penetration of a dye may vary widely with the manufacturer.

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# Physico-Chemical Studies of Extremely Basic Chromic Chlorides

*By* K. H. GUSTAVSON

In analysis of strongly basic chromic chlorides by means of the ion exchange method [1], uncharged chromium complexes were found to be the dominating constituent. Thus, preparations of the general type: $Cr_2(OH)_4Cl_2$ 4(or 2) NaCl, *i. e.*, the 33 per cent acid compound, showed about 30 per cent positively charged complexes and 70 per cent non-cationic chromium complexes. Since electro-negative complexes were not present, as shown by electrophoresis and also later by the data from analysis of the solutions by an anion exchanger of strong basic character (Amberlite IRA–400), the non-cationic fraction consisted of uncharged complexes. Their general composition corresponds to the empirical formula $(Cr_2(OH)_4Cl)$.

At the time of the first investigation, any information regarding the effect of the size of the ions participating in the ion exchange on the rate and extent of the exchange was not at hand. However, it was even then deemed desirable to check this unexpected finding of uncharged complexes as the main constituent of highly basic chlorides*(acidities: 20-33 per cent) by other methods, in the first hand by means of electrophoresis. Selective diffusion and penetration of the smaller ions may occur in exchanging ions from solutions containing complexes of greatly different size, since the diffusion of smaller ions into the interior of the resin granulae in order to reach the exchange points can readily take place, whereas large ions may be restrained, being too bulky to penetrate the micellary channels. The analysis of the 31 per cent acid compound indicated the presence of simple hydroxo-chromium cations (with compensating anions giving an acidity of the order of 66-67 per cent) corresponding to the empirical formula $Cr_2(OH)_2Cl_4$ and a predominating fraction consisting of uncharged complexes of 17 per cent acidity. In view of this, it seemed possible that part of the chromium returned as uncharged complexes by the exchange method actually consisted of cationic complexes of such large molecular size as to prevent them to enter the micellary channels and hence to reach the anionic sites of the interior of the resin.

It was shown by Samuelson [2] that in the anion exchange of lignosulfonic acids, the high-molecular fraction passed through the anion exchanger for that reason. More recently Richardson [3] has studied the effect of the size of anions of aromatic sulfo acids (dyestuffs) on their extent of exchange. He found that anions of 10 Å diameter were completely taken up by the resin, whereas only 3 per cent of large anions (30 Å) reacted. Further, Kunin and Winters [4] have recently shown that the effective exchange capacity of a sulfonic acid-type cation exchanger towards aralkyl-ammonium ions decreases with increasing ionic radii. By varying the degree of crosslinking of the resin units, it is possible by recent developments to effect separation of ions of different sizes; few crosslinks permitting exchange with large ions [5]. Hence, it is of general importance for the analysis of chromium salts by the exchange method to ascertain if this complication of molecular size is present and if it will detract from the general usefulness of the method. In addition to further investigations of the behavior of solutions of extremely basic chromic chlorides toward some new types of resins at various experimental conditions, the electro-chemical nature of these compounds has been investigated by electrophoresis in the Tiselius apparatus and by paper-electrophoresis. Further, attempts to remove the smaller ions preferentially by collagen and estimation of their molecular size by determination of the diffusion coefficients have been included in the program. This paper gives a summary of the results obtained.

*Experiments carried out by Dr. H. Svensson of the Department of Physical Chemistry of the University of Upsala in 1945.

## Experimental

The 31 per cent acid chromic chloride used in the main experiments was prepared by the addition of sodium hydroxide to a 67 per cent acid chromic chloride which in its turn was obtained by boiling freshly precipitated hydrous chromic oxide with the required amount of hydrochloric acid. The composition of the compound is given by the formula: $Cr_2(OH)_4Cl_2.2NaCl$. In some experiments a compound containing 4 NaCl was used. The stock solution contained 6 eq. Cr per liter and was heated to the boil after the addiditon of alkali. It was diluted to 15.0 g/l $Cr_2O_3$ (0.6 eq./1 Cr). This solution, prepared in 1943, was also used for the more recent experiments. Its complex composition is independent of chromium concentration.

*I. Ionic Exchange.*

(a) The percolation method.

The type of burette given in Fig. 1, used by Samuelson [6] in his pioneering work on ion exchange analysis, is most useful. (See also the apparatus of Thompkins, Khym and Cohn [7]). The hydrated cation exchanger of sulfonic acid type in an amount corresponding to 15 g. dry resin (0.2-0.4 mm. particle size) was packed into the tube of 18 mm. internal diameter, forming a column of 150 mm. height. In the general procedure 2.0 ml. of the solution of chromic salt (= 1.2 meq. Cr), diluted with 25 ml. water, was percolated through the column, followed up with water, collecting the effluent and washings in a 200 ml. volumetric flask; the whole procedure taking 10-20 min. In the filtrate,

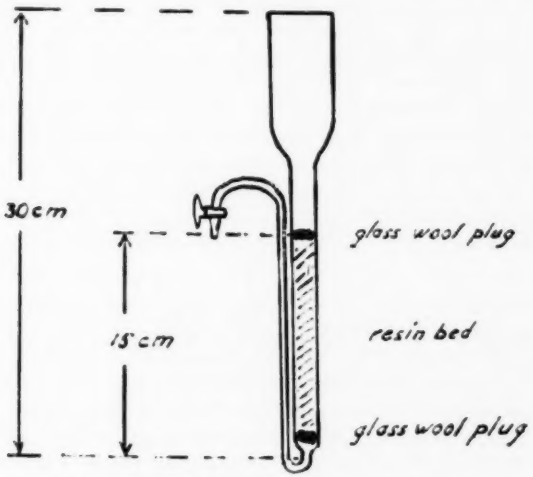


FIGURE 1.—Ion exchange column.

the content of chromium was determined. The amount of hydrolyzable chloride present in the non-cationic chromium complexes of the filtrate from the $Na^+$-charged exchanger was determined by titrating the boiling solution of the filtrate with alkali, using phenolphthalein as the indicator. For the regeneration of the exchanger 100 ml. of hydrochloric acid (1:1) was percolated through the used column for 30-45 min., washing it free from Cl-ions. The exchanger of the Na-cycle was charged by means of a 2 M solution of sodium chloride.

The cation exchangers[8] used were of two distinct types:
(a) the phenol-sulfonic acid type represented by the resin used in early years, Wofatit KS and Amberlite IR-100 H with exchange capacity of 2.4 meq. per g. dry substance and (b) resins devoid of phenolic groups with nuclear sulfonic acid groups as sole functioning groups represented by Dowex-50, a sulfonated styrene of high exchange capacity, 5.2 meq. per g. dry substance, Amberlite IR-120 and Scanotit HAF (manufactured by Höganäs-Billesholms AB, Sweden). The exchangers were used both in the $H^+$-cycle and $Na^+$-cycle. In the main experiments Wofatit KS and Dowex-50 of particle size 0.2-0.6 mm. were employed. For some additional experiment for ascertaining the influence of the particle size of the resin upon the ion exchange[9] a coarser preparate of 0.8-1.0 mm. particle size and a finely divided preparate of 0.1-0.2 mm. size were employed. Dowex-50 in the sodium form was also used as a fine powder in one experiment ($< 0.1$ mm.). It has earlier been found[10] that by decreasing particle size of the resin, the percentages of chromium taken up by the resin increases. Thus, with the coarse Wofatit KS, 28 per cent of the total chromium was removed by the resin, whereas the resin of the regular size showed 30 per cent cationic chromium and the most finely ground preparation, 34 per cent. With Dowex-50 in the form of a fine powder, the time of filtering was 2-3 hrs. Hence, it is evident that the slow flow rate limits the extent of subdivision, since in analysis of many basic chromic salts the time factor is of utmost importance, especially in analysis of solutions containing labile chromium complexes. However, by employing the resin of high degree of subdivision in the shaking method, to be described in the next section, the analysis can be carried out within a short time limit.

Analysis by the $H^+$- and $Na^+$cycles gave identical results for the basic chlorides investigated, in spite of pH differences of the effluent in the exchanger from 1.5 to 4.5. In analysis of basic chromic sulfates containing uncharged and anionic complexes in equilibrium with cationic ones, the H-form of resin gives greater removal of electropositive chromium than the $Na^+$- form[11]. This is not a depressing effect of H-ions on the ionization of the sulfonic acid group since they then should have the reverse effect to that noted. The possibility of H-bonding of non-cationic chromium on the $HSO_3$-groups of the

exchanger has been suggested as an explanation [11]. However, results of recent investigations point to the action of the liberated H-ions on the chromic salt during the exchange by means of the $H^+$-cycle as the main cause of the greater values of cationic chromium obtained in this instance; larger non-cationic complexes being changed into positively charged chromium complexes by de-olation. The proof is exemplified by investigations of the same type of basic chromic chlorides in solutions of various age and treatment. The compounds of the present study were heated after the addition of alkali and aged. Examining the 31 per cent acid chromic chlorides *directly* after addition of alkali in the cold, the H-ion exchanger gave 51 per cent non-cationic chromium whereas in the $Na^+$-cycle the corresponding figure was 67 per cent the figures of cationic chromium increasing with the duration of the treatment with H-ion charged organolite. By keeping the solution of the basic chromium chloride at 90-95°C. for one hour, subsequently ageing for 7 days, the $H^+$-cycle showed 68 per cent and the $Na^+$-cycle 70 per cent of total chromium in the form of non-cationic chromium. Evidently the acid-sensitive hydroxo- and ol-compounds in the freshly formed basic chromic chloride of non-cationic type are turned into cationic complexes in the high acid milieu of the $H^+$-charged system. The complexes of the heated solution of the chromium salt are rather inert towards H-ions. Hence, the analysis of chromium salts by means of cation exchanger should be operated in the sodium cycle.

The two phenolsulfonic acid resins showed both 30 per cent cationic chromium in the solution examined. The other types showed 32-34 per cent of the total chromium to exist as electropositive complexes. The acidity of the chloro-chromium complex of the uncharged complex was 15-18 per cent. Summing up, it can be said that the various exchangers gave concordant values of the electrochemical composition of the basic chloride.

(b) *Shaking Method*

Investigations of recent years for separating and determination of chromium complexes of different charge have been carried out by shaking the solution of chromic salt with a given amount of the resin in the sodium-charged form for periods of time from 10 min. to 2 hours. As evident from the data given in section (a), only a small fraction of the exchange capacity of the column was made use of in the column runs, generally 4-8 per cent of the exchange capacity (including all cations concerned). In the shaking modification about 1-2 meq. of chromium in a total volume of 15-20 ml. is brought to interact with a quantity of resin of 5-10 meq. exchange capacity. A similar type of procedure has been used by Theis and Thorstensen [12].

The time factor is shown by Table I, containing the results from runs with 3.0 g. moist Na-Dowex-50 (= 1.5 g. dry substance) of 8 meq. exchange capacity and 2.0 ml. of the 31 per cent acid chloride, diluted with 10 ml. water for various periods of shaking. The treated resin with its solution was then poured

on a filter inserted in a 200 ml. volumetric flask, the combined effluent and washings made up to the mark and analyzed for chromium.

TABLE I

Time factor of cation exchange

| Time | 10 min. | 30 min. | 1 hr. | 4 hrs. | 24 hrs. |
|---|---|---|---|---|---|
| % cationic chromium | 30 | 29 | 30 | 29 | 30 |
| % uncharged chromium | 70 | 71 | 70 | 71 | 70 |

Hence, a shaking time of 10 minutes is sufficient for the complete uptake of the electropositive chromium in this instance. Employing the sodium cycle of the other resins mentioned in section (a) figures of cationic chromium were in the range of 29-32 per cent of total chromium, upon interaction for one hour.

It was also of interest and importance to ascertain if the uncharged chromium complexes present in the effluent were non-reactive to the cation exchanger upon a second treatment. In order to test this point, 5.0 ml. of the chromic chloride (= 75 mg. $Cr_2O_3$), diluted with 5 ml. water was shaken for one hour with 7.5 g. moist Na-Dowex-50 (= 3.6 g dry substans) of 19 meq. exchange capacity. The effluent and washings were made up to 25 ml. It contained 53 mg. $Cr_2O_3$ *i.e.* 71 per cent of the total chromium was present in the form of uncharged complexes. 20 ml. of the filtrate (= 42.4 mg. $Cr_2O_3$) was further shaken with 6 g. moist Na-Dowex-50 and the resulting filtrate and washings made up to 100 ml. Its chromium content was 42.8 mg. $Cr_2O_3$. Thus, the non-cationic fraction had not reacted with the exchanger. This finding and earlier ones point to the non-ionic nature of the main constituent of the strongly basic chromic chlorides.

II. *Electrophoresis.* As mentioned in an earlier paper [10], the results from the early work on electrophoresis of the solution in the Tiselius apparatus were not conclusive. Solutions containing 2-11 g/l $Cr_2O_3$ were examined, using 0.01 M lithium chloride as conducting electrolyte adjusted to pH 3.5 at a current density of 8-10 mamp. and potential gradient of 3-6 v/cm. for 4-20 hours. The conductivity of the solution containing 1.4 g/l $Cr_2O_3$ was $10.68.10^{-5}$ $ohm^{-1}cm^{-1}$. It was found that all chromium migrated, although it showed different mobility, from 10 to 26 x $10^{-5}$ cm/sec. per v/cm. Dr. Svensson suggested the absorption of simple chromic cations by the larger uncharged complexes as a possible explanation of his findings. From results of series of runs carried out last year in the Tiselius apparatus by Mr. H. Nihlen of the *L. K.B. Research Laboratory*, Stockholm, the following findings are of interest. The 31 per cent acid chloride, $Cr_2(OH)_4Cl_2.4$ NaCl in a concentration of 3.8

g/l $Cr_2O_3$, was examined in 0.1 M lithium chloride solution of pH 3.5, equal to that of the solution of chromic chloride, which had a conductivity of $8.87 \times 10^{-4}$ $ohm^{-1} cm^{-1}$; that of the lithium chloride solution was 4.86 units. The potential gradient was 2.11 v/cm and time of electrophoresis 4 hours. Fig. 2 shows the displacement of the boundaries after 4 hours. The diagram of the ascending left arm shows a symmetric top which does not move, or only slightly so, and another component moving with a mobility of $22.5 \times 10^{-5}$ cm/sec. per v/cm. The diagram of the descending right arm shows also a non-moving top and a larger top of two components which showed mobilities of 19 and 15 of the units given. The presence of chromic complexes of low or no mobility is thus indicated.

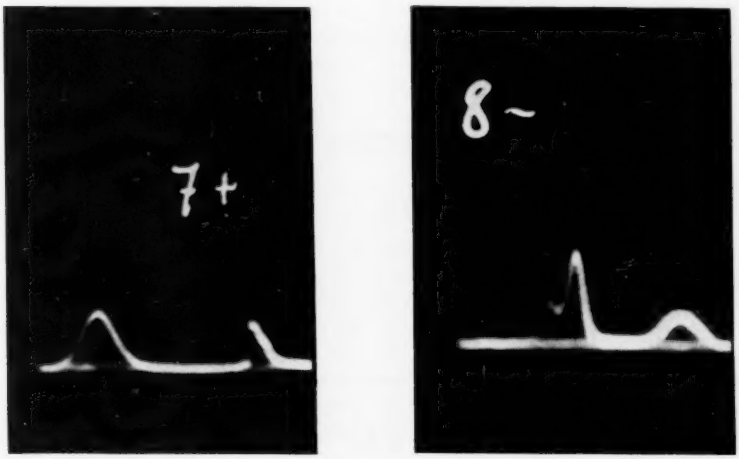


FIGURE 2.—Electrophoretic diagrams after 4 hours (Tiselius apparatus).

In the photographic registration of the boundries of the various constituents by this mode of electrophoresis, false tops due to the salt make the interpretation of the diagrams difficult at times. Hence, the recently developed paper-electrophoresis method [13] was tried.

The drawings in Fig. 3 show the simple apparatus used; a simplified type of the apparatus constructed by Tiselius [14]. It is assembled from two battery jars(A), two 8 mm. thick glass plates (B) of equal size (28 x 10 cm.), two U-tubes (C) and two carbon electrodes (D). The battery jar is divided into two equal parts. The jars are filled with the conducting solution, 0.1 M solution of sodium chloride adjusted to pH 3.5 by hydrochloric acid. The halves of the jars are connected by means of the U-tubes. The glass plate is placed

between the jars. A thin coat of Dow-Corning stop cock grease is applied evenly on the upper surface of the glass plate. On a heavy filter paper, Munktell special, 36 x 9 cm, a few drops of the solution of the chromic salt is applied on the center of the paper (2–5 mg. $Cr_2O_3$). After light drying (2–3 min.), the paper is carefully wetted by passing it through the sodium chloride solution quickly. It is then put on the glass plate, leaving the ends of the paper dipping down in the solution of the inner compartments of the jars. Care should be taken to eliminate air bubbles between glass and paper. The silicone greased surface of the other plate is pressed on the paper. The paper is hence held airtight between the plates. Heavy silicone grease is applied on the side cross section of the glass-plates. The two carbon electrodes inserted in the outside compartments of the jars are connected to a circuit from 220 v. D.C. containing a suitable rheostat and a combination volt-amperemeter, yielding a current of 10–20 milliamps.

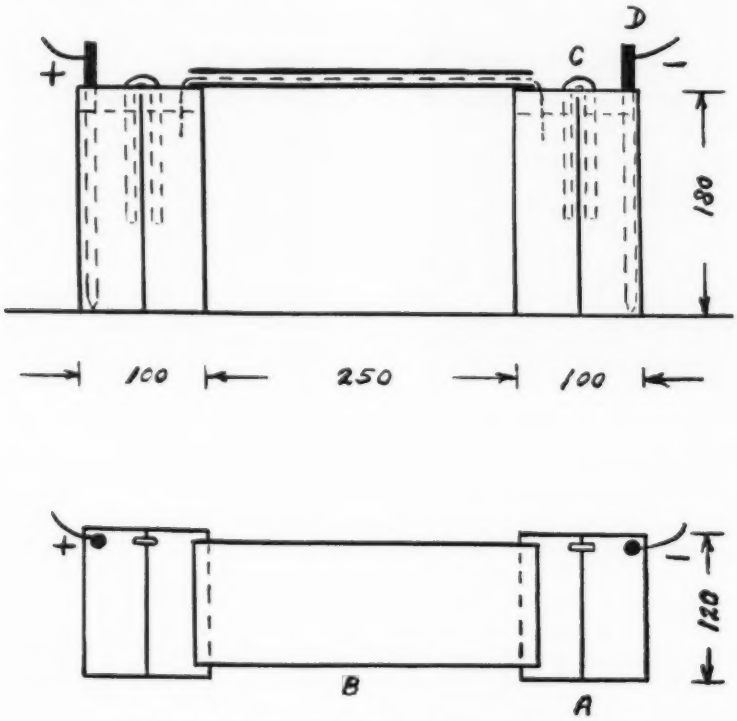


FIGURE 3.—Apparatus for paper-electrophoresis (Tiselius).

A spot of a normal chloride (5 mg $Cr_2O_3$) will reach the end of the plate upon 3 hours, moving as a fairly uniform band. The basic chlorides of acidities >50 per cent give as a rule a streak of chromium with the largest part in the most rapidly migrating part, the front. The paper is dried at 50–60°C. and examined. For quantitive analysis the dried paper is cut in sections. The chromed paper is ashed, and oxidized. To the acidified solution diphenylazide is added and the chromium content determined spectrophotometrically in a Spekker spectro-absorptiometer. Fig. 4 shows the contrast photograph A of the migration of 4.8 mg $Cr_2O_3$, applied as 3 drops of 67 per cent acid chromic chloride, 50 g/l $Cr_2O_3$, after 3 hours and B the corresponding run with 5.2 mg $Cr_2O_3$ applied in the form of 31 per cent acid chromic chloride, 50 g/l $Cr_2O_3$. The more acid chloride leaves only faint amounts of chromium on the paper within the zone of 8 cm distance from the spot of application. The main part of chromium is present in the extended streak located 8-16 cm from the spot and smaller amounts in the front, about 20 cm from the spot. In analysis of the chrome content of papers from this solution, about 90 per cent was found in the large streak and 8 per cent in the fastest moving front. The picture of B shows clearly the very slow migration of chromium in the 31 per cent acid chromic chloride. Analysis of the papers shows average values of 30-40 per cent non-migrating (unchanged chromium); about 40 per cent in the fastest moving fraction and 20-30 per cent in the intermediate zone.

Possible complications due to adsorption of components of the basic chromic salt and electrostatic effect of the electrolyte added may occur and these aspects have not been investigated yet. However, it has been found to be imperative not to dry the paper too long or by heat after applying the solution to be analyzed on the paper, since the spotted paper will then be difficult to wet and part of the chromium will remain in the spot irrespective of its charge. The data show that the extremely basic chromic chlorides contain a considerable part of complexes with very low or hardly any cataphoretic power. The simple method described will likely be of great help in investigating many aspects of tanning problems.

III. *Interaction with collagen.*

It has been found that in treating *pelt* with solutions of extremely basic chlorides, a preferential fixation of the cationic complexes occurs. The following experiment gives an illustration. A portion of squeezed neutral delimed pelt (belly of a cow hide; 1.5 cm. thick) equal to 6.2 g. collagen was shaken for 12 hours with 50 ml. of the chloride containing 7.5 g/l $Cr_2O_3$. The exhaust contained 4.8 g/l $Cr_2O_3$ and its acidity was 20 per cent; with final pH 4.1. The analysis of the exhaust by ionic exchange gave 87 per cent uncharged chromium and 13 per cent cationic complexes. The stock which was partially case hardened, due to the surface fixation of the larger aggregates probably, was pressed *without* washing and weighed (16.1 g.). Its dry

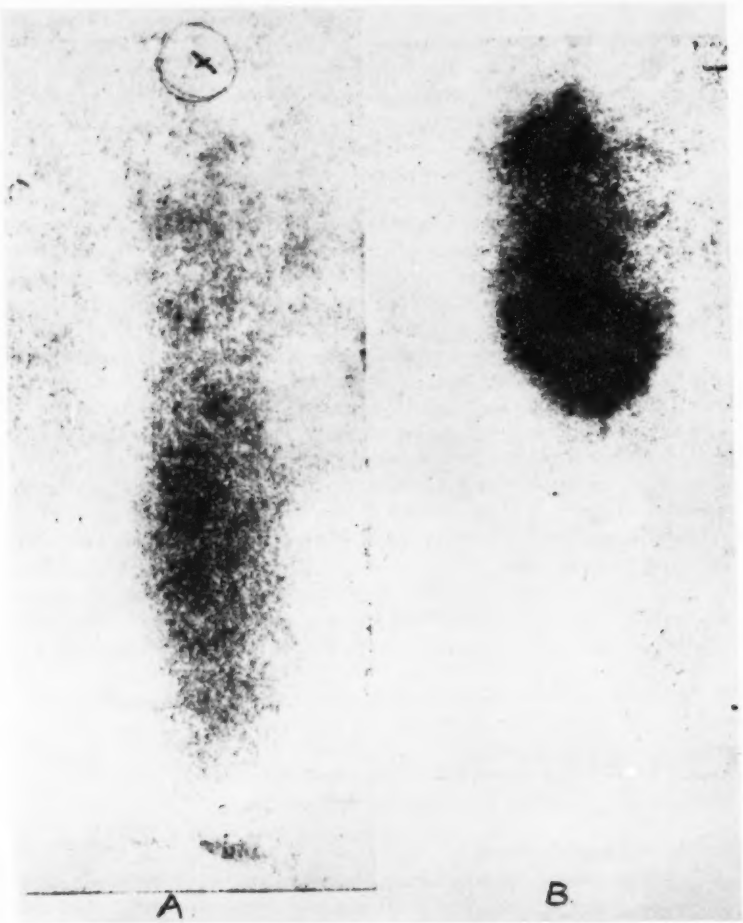


FIGURE 4.—Contrast photographs of the papers after 3 hours electrophoresis.
A. 6% acid chrome chloride.
B. 3% acid chrome chloride.

weight was 6.25 g. Hence it contained 8.55 ml. water of which 1.25 ml. (20 per cent of 6.2 g) was assumed to be in the form of water of hydration [15] and the rest, or 7.3 ml. present as residual solution. The amount of chromium therein was hence 7.3 x 0.0048 g. = 0.035 g. $Cr_2O_3$ or 0.6 per cent $Cr_2O_3$ on the

weight of collagen. Hence the percentage of fixed $Cr_2O_3$ on the basis of collagen amounted to 1.7 per cent. The acidity of the final chrome-collagen compound was 62 per cent.

The balance of the reaction, including the uptake of cationic and uncharged chromium by pelt, and the determination of fixed chromium are shown by data from analysis of the original and residual solutions given in Table II.

TABLE II

Balance of chrome between pelt and solution

| | mg $Cr_2O_3$ as cations | mg $Cr_2O_3$ in uncharged form |
|---|---|---|
| In original solution | 113 | 262 |
| In residual solution | 36 | 238 |
| Fixed by pelt | 77 | 24 |
| % $Cr_2O_3$ on collagen | 1.2 | 0.4 |

The total chrome fixation was hence 1.6 per cent $Cr_2O_3$, based on collagen by the indirect method. It is to three fourth composed of cationic chromium, showing the preference of collagen for the smaller, less basic constituent of the chloride. A heavy compact substrate was intentionally selected for this experiment in order to decrease the uptake of the larger complexes (uncharged) by collagen and thus to bring about a partial separation of the two main constituents. With hide powder the particle size will favor the uptake of the very basic chloride and thus, in tanning experiments with hide powder 10.1 per cent $Cr_2O_3$ was fixed by collagen consisting of about equal parts of the two types of complexes; 8 per cent accidity of the chloro-chromium complexes fixed by collagen.

It is interesting to note that the acidity of the chrome collagen compound was 62 per cent, whereas the acidity of the non-reacting fraction was 20 per cent which figures are in good agreement with the values obtained by the ion exchange technique indicating the presence of a 67 per cent acid chromic chloride (cationic) and an uncharged fraction containing chromium complexes of acidities in the range 16 - 18 per cent. It has also been demonstrated in earlier investigations[16] that the present type of chromic chlorides is more extensively fixed by heat-denatured hide powder than by natural hide powder which is conceived to indicate participation of non-ionic valency forces in the fixation or complexes of large size. Chromic chlorides of acidities >60 per cent which contain cationic chromium entirely, show the same affinity to both types of hide powder. (electro-valent reaction).

IV. *Precipitation of gelatin solution.*

A common property of chromic chlorides is their great solubility in ethanol, which fact also is in line with their less pronounced electrolytic nature. The

chromic sulfates are insoluble in ethanol. Another exclusive character of solution of the extremely basic chromic chlorides is shown by their property of forming insoluble precipitates with gelatin solutions. Chromic sulfates and chromic chlorides of acidities >50 per cent do not show this reaction which has been noted by Küntzel [17] earlier.

The following simple experiment illustrates this point. To 10 ml. of a 1 per cent solution of gelatin, a quantity of 2 ml. of the 31 per cent acid chromic chloride, 15.0 g/1 $Cr_2O_3$, was added under shaking (3 per cent $Cr_2O_3$ on the weight of the protein). A heavy precipitate was formed which was freed from the bulk of the solution by filtering through a glass filter. The precipitate contained about 60 per cent of the original amount of chromium. Practically complete removal of chromium by gelatin is obtained in systems of low percentages of chromium on protein if sufficient time is given for the interaction, due to gradual fixation of cationic chromium by the protein. The precipitation also takes place with gelatin adjusted to pH 3.5 with hydrochloric acid and hence apparently it is not due to the formation of insoluble, still more basic chromic chlorides resulting from disturbed hydrolytic equilibrium by removal of acid by the protein as Küntzel believes. It is probably a case of crosslinking gelatin chains by means of coordinated uncharged chromium complexes. By having the basic chloride diffuse into a 5 per cent gelatin gel, set in test tubes, a separation of the two main types of chromium complexes is also feasible. (*Cf* [17]).

V. *Determination of the diffusion coefficients.*

An account will also be given of the results obtained in determination of the diffusion coefficients of the present type of chromic chlorides, carried out by G. Ekström in 1945–1946. This work was initiated with the view of obtaining some idea about the molecular size of the complexes, found to be uncharged by the ionic exchange method with due regard to the possible interference of the molecular size on the uptake of these complexes by the cation exchanger. Upon four weeks' dialysis of a solution of a 28 per cent acid chromic chloride containing 1.7 eq/1 Cr, of which 78 per cent were uncharged, in a cellophane bag, against water, 91 per cent of the chromium had dialyzed. Its average acidity was 30 per cent. An amount of 9 per cent of the total chromium was left in the dialysator. Its acidity was 14 per cent. Hence, this solution contained a small part of highly aggregated complexes.

Measurements of the diffusion coefficients by means of the Northrop–Anson-McVain method [18] gave an average value of D = 0.27 upon 168 hours' dialysis which should mean an average molecular weight of about 600 for the 28 per cent acid chromic chloride. That would correspond to compounds of the type $(Cr_4O_6(OH_2)_{12}Cl_2)$. With increasing duration of the dialysis, the diffusion coefficient decreased, indicating the presence of complexes of widely different size in this solution. A 30 per cent acid chloride, 0.6 eq/1 Cr, freed from sodium

chloride by means of ethanol, precipitating the chromic compound by ethyl ether and redissolving the solid product in ethanol, gave D = 0.35, corresponding to an average molecular weight of 340. The data obtained showed a high degree of irregularity and hence little importance should be attached to these findings. Further work, including measurements by means of the ultracentrifuge, will be undertaken in order to settle this problem. However, the trend of the data does not indicate the presence of very large complexes in any great amounts.

## Concluding Remarks

It is known from the important investigation of Bjerrum and Faurholt [19] on the constitution of extremley basic nitrates and chlorides of chromium, that upon boiling the solution some hexaquo-chromium ions are formed, on the one extreme, and aggregated more highly basic compounds, on the other extreme. The data of the composition and behavior of the 31 per cent acid chromic chloride studied indicate the presence of two main types of components: (1) positively charged complexes, probably of various degrees of charge, forming with their compensating anions salts of average acidity in the vicinity of 67, corresponding to $Cr_2(OH)_2Cl_4$ and (2) the main constituent, consisting of uncharged complexes with chloro-groups complexly bound, with one atom of chlorine on two atoms of chromium on the average. The electrochemical makeup of the extremely basic chromic chlorides is independent of the chrome concentration of the solution and the uncharged complexes are rather stable. The findings of the ion exchange investigation are in agreement with the results of this study. Hence, it is indicated that the large percentages of chromium returned as uncharged complexes are not a matter of shortcomings inherent in the technique, due to the presence of cationic chromium complexes of such large size as to prevent their participation in the ion exchange. An answer to that problem was actually the main issue of the present investigation.

In contrast to the relatively high degree of stability of the uncharged chloro-chromic compounds, the corresponding cationic chloro-compounds of basic chlorides are exceedingly instable, the acido group being easily displaced by changed hydrolytic equilibrium, for instance by dilution of the solution or by lowering the concentration of Cl-ions [1]. The basic sulfates of chromium show the reverse trend: the cationic sulfato complexes are rather stable whereas the uncharged and negatively charged sulfato-complexes of basic sulfates are very labile [1]. Hence, it is evident that the sign and size of the electric charge of the chromium atom and the nature of the anion, and hence the acido groups, markedly influence the stability of the complexes.

## Acknowledgment

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due to the collaborators mentioned in the text as well as to *Dr. S. Brohult*, L. K. B. Research Laboratory, Stockholm and *Dr. C. E. Danielsson*, Institute of Biochemistry, Upsala.

## Summary

Analysis of solutions of extremly basic chlorides of chromium with composition corresponding to the empirical formula: $Cr_2(OH)_4\ Cl_2 2\ NaCl$ by means of five different cation exchangers of sulfonic acid type, operated in the sodium and hydrogen cycles, show the compounds to contain 30 per cent of the total chromium as cationic complexes and 70 per cent as uncharged complexes. The former with their compensating anions form a salt of about 67 per cent acidity ($Cr_2(OH)_2Cl_4$). The acidity of the uncharged complexes is of the order of 16 - 17 per cent ($Cr_2(OH)_5Cl$). The $H^+$-and $Na^+$-resins give identical results.

By free electrophoresis, complexes of different mobilities are found. The results are somewhat inconclusive. By means of paper-electrophoresis, the presence of a non-migrating portion is proved and also slow-migrating complexes in addition to cationic complexes of greater electrophoretic migration.

Interaction of solutions of the basic chloride with collagen (heavy pelt) leads to removal of the simple cationic chromium complexes by their preferential fixation by collagen, leaving a greater proportion of uncharged complexes in the residual solution.

Solutions of these strongly basic chlorides form precipitates with gelatin solutions. Measurements of diffusion coefficients show values corresponding to molecular weights of the order of 400–600 in these solutions.

Garverinäringens Forskningsinstitut,
Stockholm, Sweden

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# Enzyme Evaluation by Viscosity Reduction*

By R. F. Nickerson†

*A. C. Lawrence Leather Co.*

## Enzyme Evaluation by Viscosity Reduction

The bating process is well known to have beneficial effects on grain appearance and to increase the porosity or openness of leather. Proteolytic enzymes play a leading role in this process and there is evidence that the enzymes in conjunction with deliming salts also facilitate deliming and cause a greater falling of limed stock than do deliming salts alone. Apparently, proteolytic enzymes of pancreatic origin as well as some from bacterial and fungal sources are satisfactory in bates.

The mechanism by which proteolytic enzymes produce bating effects is not known with certainty. The effects are roughly proportional to the product of enzyme concentration and time of bating. However, means of determining the progress of bating are entirely subjective so precise data that might help explain the process are not available.

The present investigation was undertaken with the determination of proteolytic enzyme activity as the objective. With enzyme activity known it seemed possible that the bating process might be studied with some insight. In view of the limited knowledge of the bating process, the variety of suitable proteases, and the known action of proteases, it may be assumed that any method of assay which measures the ability of the enzyme to sever peptide bonds is adequate for test purposes. A number of commercial bate producers employ a casein digestion method.

*Presented at the Forty Seventh Annual Meeting, Groton, Conn., June 11, 1951.
†Present address Monsanto Chemical Co., Everett, Mass.

The method of assay described in this paper may be of interest because it is sensitive, has fair accuracy and requires only limited equipment. It is based on the rate of reduction in viscosity of a gelatin sol.

Orthmann, Surak and Koch [1] reviewed the literature on bate evaluation methods including those which depend upon casein, keratose, elastin, collagen and gelatin as substrates and concluded that the similarity between gelatin and hide substance favored the use of gelatin. Apart from the fact that this conclusion involves an unjustified assumption as to the mechanism of bating, it can be shown that the interpretation of their experimental viscosity data is based on a false assumption which may introduce considerable errors into their estimates. Koch, Orthmann and Degenfelder [2] subsequently modified the apparatus and method of calculation, and improved the reliability of the results but apparently did not recognize the nature of the improvement.

The more recent publications concerning gelatin as a substrate yield some new information. Vlcek and Mansfeld [3] proposed a modification of previous methods and followed the viscosity changes with time with a Höppler Viscometer. A gelatin concentration of 5 to 6 per cent at 40°C. was preferred. Anderson [4] claimed that proteolytic anaerobes have excellent bating powers when they are used in proportion to their ability to liquefy gelatin. Lennox [5] measured the gelatinase activity of a number of proteases and concluded that the time for a given viscosity change bears no constant relationship to concentration of enzyme over a wide range of enzyme concentrations. Enzyme activity was, therefore, taken as the reduction in viscosity produced in 10 minutes at 40°C. as a fraction of the initial viscosity. Lennox's method of calculation like that of Orthmann, Surak and Koch may lead to appreciable errors.

Gelatin is a high polymer and as such its viscosity may be considered in the light of Staudinger's investigations and the recent work of others. A sensitive measure of chain length and now widely used for determination of degree of polymerization, viscosity is subject to accurate measurement with relatively simple equipment. It is well known, however, that viscosity is directly proportional to chain length only in very dilute solutions and frequently only where special solvents are used. At the relatively high polymer concentrations involved in enzyme assay work viscosity is an exponential function of polymer molecular weight and appreciable errors must result if a linear relationship is assumed.

The advantages of gelatin as a substrate are that it forms reasonably homogeneous sols, is widely available in a granular form of high purity for bacteriological work, exhibits the characteristic viscous behavior of high polymers, and stays in solution over the entire pH range. It was finally adopted when a reliable method of calculation was worked out.

*Theory.* Since the total solids concentration remains practically unchanged during the viscosity reduction process, it is assumed the changes occurring

are the result primarily of decreases in degree of polymerization of the gelatin. Each viscosity value in the range involved is assumed to represent an average degree of polymerization together with a characteristic amount of molecular association which depends upon chain length, temperature and total solids concentration. At constant temperature and total solids concentration especially in an enzyme degraded system, it is expected that association effects would be fixed and that viscosity would be a function of chain length. From this point of view enzyme activity should be taken as the reciprocal of the time for a specific change in viscosity but with a further restriction. The limits between which the specific change occurs should be arbitrarily assigned and then used with rigid adherence. Preferably the upper viscosity limit assigned should be somewhat below that of the initial gelatin sol. By this means spurious effects at the initiation of the process, such as temperature imbalance and incomplete mixing, are avoided and, furthermore, the system is brought to a replicative condition. That is, the initial viscosity of the gelatin sol may result from chains of fairly uniform length compared to average length, from mixtures of very long and very short chains or from intermediate mixtures. Partial degradation of these systems by an enzyme should make them more similar to each other in chain length composition and viscous behavior.

The variation of viscosity with time during the enzymic process of hydrolysis has been recognized as hyperbolic [1, 5] and this type of curve was obtained in present experiments. However, Orthmann, Surak and Koch [1] interpreted some of their results as indicating "that the amount of enzymic material is not as important as has been assumed". They also suggested that the rapid drop in viscosity at the outset of the process shows great activity of the bating material in the first part of the reaction, that, thereafter, the reaction rate seems to decrease and the curve to flatten out, and that "probably this deviation from the law of kinetics is due to the inactivation of the bate because of the products of hydrolysis formed, reverse reaction, inhibition, poisoning, etc." An experiment described later fails to confirm this explanation.

*Apparatus.* Viscosity measurements are made in a bath at 38°C. on a 4 per cent gelatin sol with a capillary discharge viscometer of 10 ml. capacity. The viscometer is lowered into the enzyme-gelatin solution, filled by suction, raised out of the liquid, and allowed to drain. Drainage time between marks is measured with a stop watch and elapsed time is noted on a pocket watch when the meniscus passes a mark which represents one-half the drainage time. The viscometer is designed to fit into cloud-and-pour-point test jars.

The choice of conditions and apparatus is probably not critical and can be altered somewhat as the need may require provided that accuracy is not sacrificed.

*Materials*: The following materials and methods of preparation are employed but modifications can be made as required.

*Gelatin.* Make a 5 per cent solution of gelatin by weight by weighing the requisite amount of granular gelatin and adding exactly 19 parts of cold distilled water saturated with chloroform. Allow the gelatin to soak for 30 minutes at room temperature, then for 15 minutes at 38°C. and finally melt the mass by raising the internal temperature briefly to 50°C. Then place the flask in the thermostat at 38°C. and after 20 minutes transfer 20 ml. aliquots to clean dry pour point test jars. Stopper the test jars and hold in refrigerator for use.

*Enzyme.* Place 5 ml. of molar sodium bicarbonate and 25 ml. of distilled water in a 100-ml. beaker. Weigh out and add to the beaker bate approximately equivalent to 100 mg of technical trypsin, i.e. 2 to 5 grams of proprietary bates. Adjust the pH of the solution to the desired value with the Beckmann by dropwise additions of molar sodium carbonate. Deliming salts do not interfere in the final determination. Make the solution to 100 ml., shake thoroughly several times and use the clear supernatant for test purposes.

Prepare 0.625 molar phosphate buffer from disodium phosphate, using enough sodium hydroxide so that 2 ml. of the buffer in 20 ml. of 5 per cent gelatin gives the desired pH, i.e. 8, 8.5, 9 etc.

*Procedure.* Melt a 20 ml. aliquot of the gelatin by raising the internal temperature to 45° C. in a water bath. Add with stirring 2 ml. phosphate buffer and 2 ml. water. Transfer test jar to thermostat at 38°C. and after 10 minutes introduce 1 ml. of previously warned enzyme solution. Note the time. Insert the viscometer also previously warmed and measure the drainage time every 5 minutes for 25 minutes. The viscometer, thoroughly drained, may now be transferred directly to the next test jar prepared between readings for a new determination.

*Calibration of Instrument.* Drainage or efflux time values for a viscometer may be used for calculation of results but this procedure is not recommended. The instrument constants can be obtained readily by use of standard reference oils of known viscosities (Bureau of Standards) or of sucrose solutions[6]. The latter were used in the present work. When this calibration is made, several viscometers can be employed on a comparable basis in the same or in different laboratories.

The formula for the capillary discharge type of viscometer is:

$$N = \frac{100d\,(f - \frac{K}{f})}{C} \qquad (1)$$

in which

N=kinematic viscosity in centipoises
f=efflux time in seconds
d=density of liquid in gm. per ml.
K and C=instrument constants

To determine the instrument constants, it is necessary only to measure the efflux times, f, of two liquids of known viscosity and density and to substitute the appropriate data in the above equation. The equations so obtained can be solved for K and C.

*Derivation of Working Formula.* It frequently happens, as in the present case, that the substance of principal interest is a solid which can be dissolved in an inert solvent. Both solute and solvent make contributions to the viscosity of the solution and it is desirable to minimize the influence of the solvent. This is often done by calculation of specific viscosity, Nsp, as follows:

$$Nsp = \frac{N_G - Nw}{Nw} \tag{2}$$

in which

$N_G$=viscosity of solution
Nw=viscosity of solvent

For present purposes $N_G$ is the viscosity of aqueous gelatin sol and Nw is the viscosity of water.

The fall in viscosity of a gelatin sol produced by a proteolytic enzyme is nearly hyperbolic with time as was mentioned above. It is also shown in Figure 4 of this paper. An important observation in the present work was that a plot of the reciprocal of viscosity against time is nearly linear as can be seen in Figure 5. The reciprocal of viscosity is called *fluidity*. It should be noted that fluidity *increases* as viscosity *decreases*.

Actually *relative fluidity* is used and the derivation of the final working equation is given below. First, Equation 2 is inverted and yields

$$F = \frac{Nw}{N_G - Nw} \tag{3}$$

in which F is fluidity. Now, the fluidity of a standard gelatin sol containing no enzyme but diluted to the concentration which would result if enzyme were added can be expressed in terms of Equation 3 as

$$Fo = \frac{Nw}{N_{Go} - Nw} \tag{4}$$

In this equation the subscript o's indicate zero time. That is, Fo is the fluidity of the gelatin sol the instant the enzyme has been added but before the enzyme has begun to act. After the enzyme acts for time, t, fluidity becomes

$$F_t = \frac{Nw}{N_{Gt} - Nw} \tag{5}$$

Relative fluidity, $F_R$, is simply the ratio of fluidity at time, t, to fluidity at zero time, i. e.

$$F_R = \frac{F_t}{F_o} = \frac{N_{Go} - Nw}{N_{Gt} - Nw} \qquad (6)$$

In practice, where several $N_{Gt}$ measurements are made periodically on a gelatin sol, a series of $F_R$ values can arise from them by calculation.

A conversion graph can be prepared to obviate the need for laborious computations. From this graph relative fluidities, $F_R$, can be found directly from observed efflux times, f. Several simple steps are involved in the establishment of such a graph from Equation 6. First, $N_{Go}$, the initial standard viscosity of gelatin sol is determined by substituting water for enzyme but otherwise following the normal procedure. In the present case at 38°C., $N_{Go}$ was 3.905 and the viscosity of water, Nw, at this temperature is 0.678. Substitution of these data in Equation 6 gives

$$F_R = \frac{3.905 - 0.678}{N_{Gt} - 0.678} = \frac{3.227}{\frac{100d}{C}\left(f - \frac{K}{f}\right) - 0.678} \qquad (7)$$

Then, substitution of numerical values of C and K for the viscometer in question and of solution density (d = 1.02) in Equation 7 reduces it to a simple relationship containing only f and $F_R$ as unknowns. Substitution of a series of efflux times, f, in this final equation permits the calculation of a corresponding series of relative fluidity values, $F_R$. Finally, the $F_R$ values so obtained are plotted against the f values from which they arose.

The conversion graph for a viscometer used in the present experiments is shown in Figure 1. The relative fluidity corresponding to any observed efflux time can be read directly from this curve.

*Experimental Data.* The practical operation of the method is illustrated by the digestion of gelatin sol with technical trypsin. The procedure described above was followed and yielded the enzyme digestion times and viscometer efflux data shown in Table I. The relative fluidities obtained from the efflux values by use of Figure 1 are also included in the table.

TABLE I

Digestion of Gelatin Sol with Trypsin (1 mg. trypsin in 25 ml. of 4% gelatin sol at 38°C and pH = 8.)

| Digestion Time-min. | Efflux Time (seconds) | Relative Fluidity |
|---|---|---|
| 4.8 | 138.3 | 1.38 |
| 9.9 | 121.1 | 1.69 |
| 14.8 | 110.2 | 2.00 |
| 19.8 | 102.6 | 2.28 |
| 25.0 | 97.2 | 2.53 |

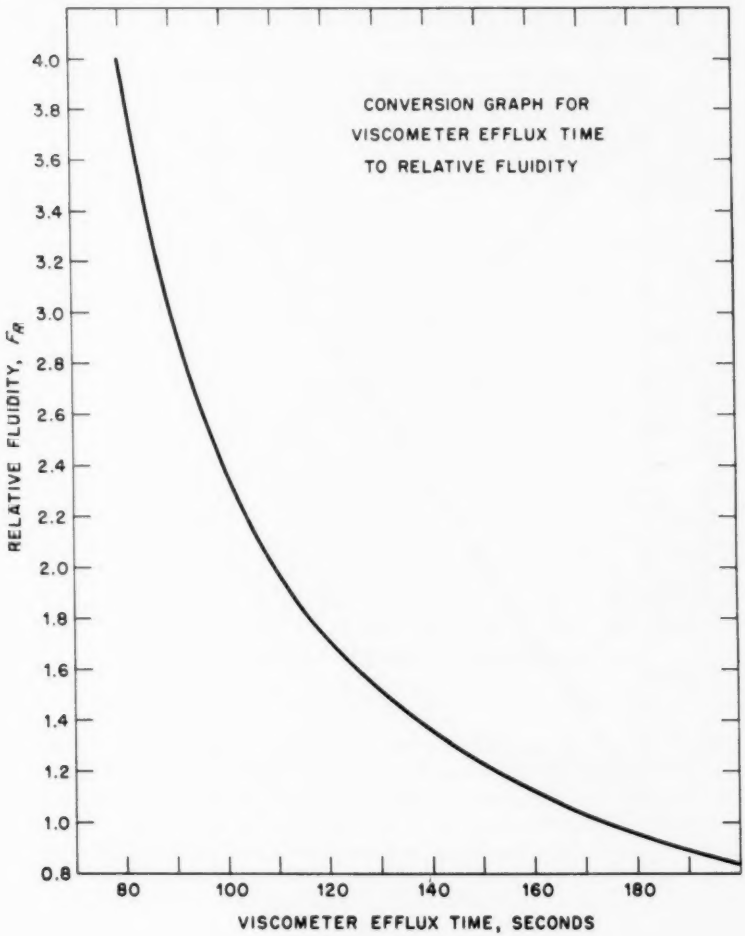


FIGURE 1.

The relative fluidity and digestion time data of Table 1 are plotted in Figure 2 and a line has been drawn through the points. The slope of this line is the rate of change of fluidity, i. e.

$$\frac{2.59 - 1.10}{25} = 0.060$$

The rate thus found is taken to represent the proteolytic activity of 1 mg. of trypsin under the conditions of test.

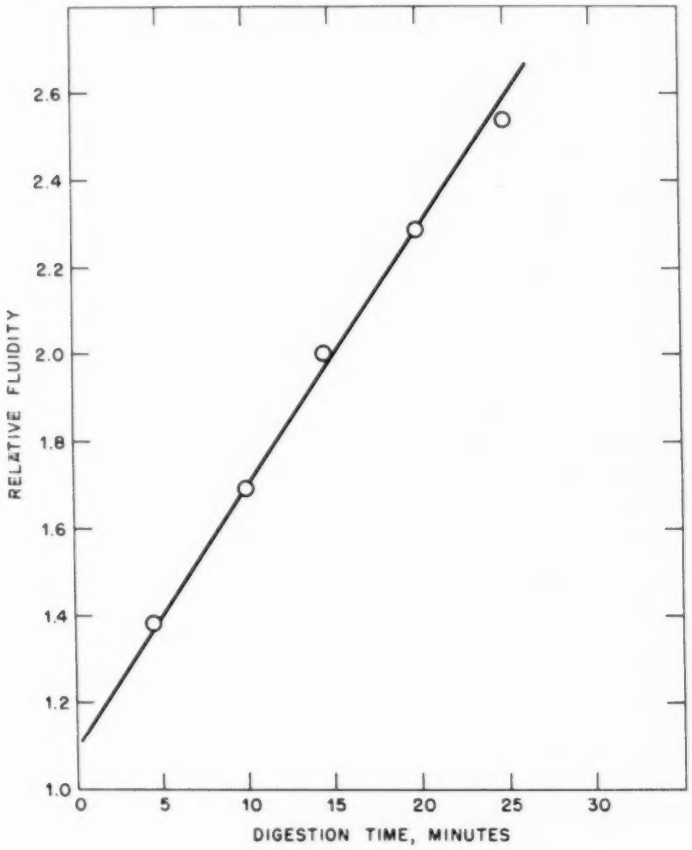


FIGURE 2.

Rates similarly determined for varying amounts of a commercial enzyme concentrate are presented in Figure 3. The graph shows that within experimental error the observed rates are directly proportional to the amounts of enzyme concentrate taken. This linear relationship gives some assurance that rates are indeed a measure of enzyme activity. It may be of interest to note that between 7 and 8 mg. of commercial concentrate are required to produce a rate equal to that of 1 mg. of trypsin.

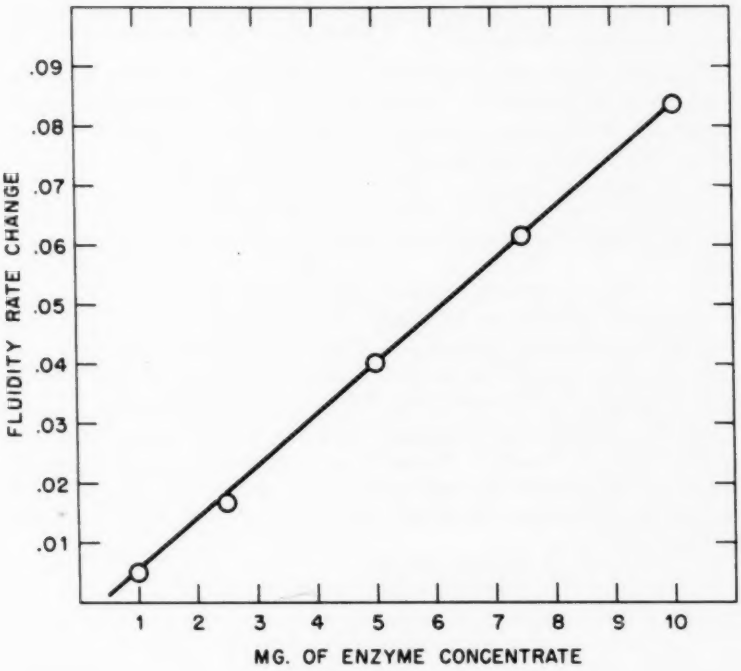


FIGURE 3.

The results of a particularly informative experiment are summarized in Figure 4 and 5. The data for these graphs were obtained as follows: First, 4% gelatin sol was run in the usual way with 2.5 mg. trypsin at 38°C and pH = 8. Then, after 45 minutes when digestion was well advanced, a portion of the digested sol representing 0.25 mg. trypsin was transferred to fresh gelatin sol. Efflux times were determined periodically on this "transplant" for about an hour. And finally, after the original sol containing 2.5 mg. trypsin had digested for 2 hours, a second transfer was made from it to another fresh portion of gelatin sol, and efflux times were again determined over an hour period.

The efflux times for the three runs just described were converted to centipoise viscosities by means of Equation 1. The viscosities so found are plotted against digestion time in Figure 4. Curve A represents 2.5 mg. trypsin while Curve B represents the two "transplants", of 0.25 mg. trypsin each. Curve C shows the behavior of gelatin without enzyme. It is apparent that 2.5 mg.

trypsin causes a rapid viscosity reduction and a tendency to level off becomes manifest in 15 to 20 minutes.

To interpret these curves it is sufficient to determine the time required for the same viscosity change to occur in each case. For example, the specific change indicated by the dotted lines on Figure 4 is from 3.6 cps to 2.4 cps. The times required for this change to take place are:

| | |
|---|---|
| 2.5 mg. trypsin | 5.0 – 0.3 = 4.7 minutes |
| 0.25 mg. trypsin | 57.5 – 6.5 = 51 minutes |

The rate of change is the reciprocal of the time for the specific change to occur, i. e.

rate for 2.5 mg. trypsin is $1/4.7 = 0.213$
rate for 0.25 mg. trypsin is $1/51 = 0.0196$

These final figures, then, are measures of proteolytic activity in the two cases and it is evident that 2.5 mg. trypsin exhibit about 10 times as much activity as 0.25 mg. trypsin. The significance of this result is discussed below.

The data in Figure 4, are replotted in Figure 5 after conversion of viscosities to relative fluidities. A comparison of the two figures clearly shows the advantage gained by the conversion. Calculation of the slopes or fluidity rate changes by the method already mentioned yields the following values for Figure 5:

| | |
|---|---|
| 2.5 mg. trypsin | 0.165 |
| 0.25 mg. trypsin | 0.016 |

Again, 2.5 mg. trypsin exhibit just about 10 times as much proteolytic activity as do 0.25 mg. It is clearly an advantage of the latter method of finding rates that a visual fit is made to a series of points. This yields an average rate as estimate of enzymic activity.

## Discussion

The data presented in Figure 4 and 5 are of considerable interest in view of some of the literature summarized in the first part of this paper. The estimates of proteolytic activity are in proportion to the amounts of enzyme represented. In other words, the present experiments yield no evidence that the amount of enzymic material is unimportant or that any inactivation of the enzyme by hydrolysis products seems to occur.

It might, at first, be assumed from the shape of Curve A in Figure 4 that enzymic activity decreases with time. However, the transfers made to fresh gelatin sols indicate that enzymic activity is unaltered even after more than 90 minutes' contact between the enzyme and the gelatin hydrolysis products. This means that proteolytic activity is the same at every point on Curve A. The shape of Curve A is, therefore, not an indication of changing enzyme activity but rather is an indication that as gelatin is cut into more and more fragments of smaller and smaller size, a longer time is required for a specific

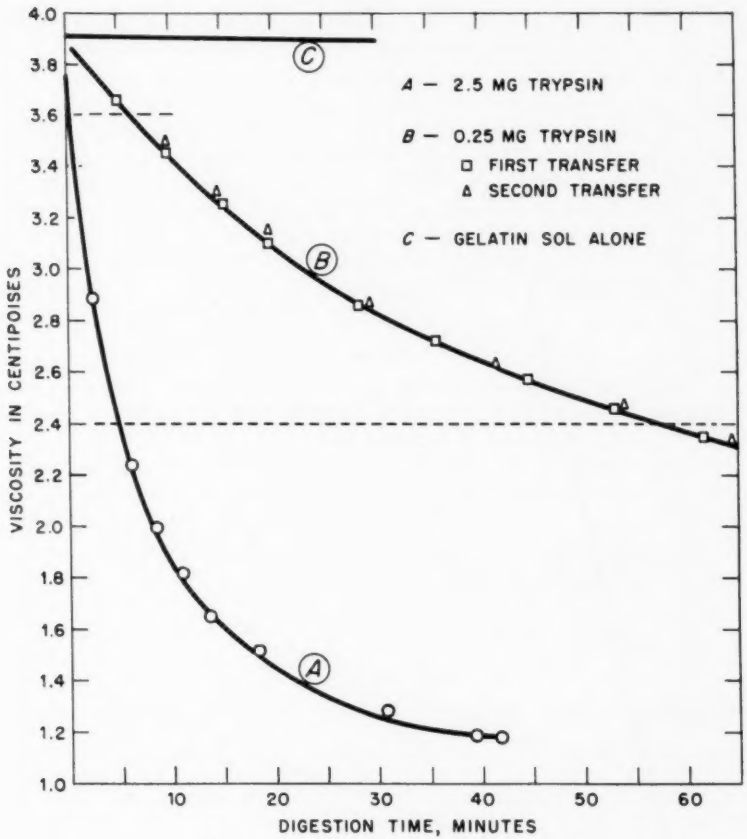


FIGURE 4.

change in viscosity to occur. It follows, then, that both a specific change in viscosity and the limits between which this change may occur must be specified if valid estimates of enzyme activity are to be obtained.

The use of relative fluidities is designed to refer all measurements to a standard gelatin sol. Obviously, a relative fluidity of 1 means that the sol in question has the same fluidity as the standard sol. In general, the preferred working range of relative fluidities should be from 1 upwards. Use of this range has the effect of starting all enzyme determinations at the same initial gelatin viscosity as is required for valid results.

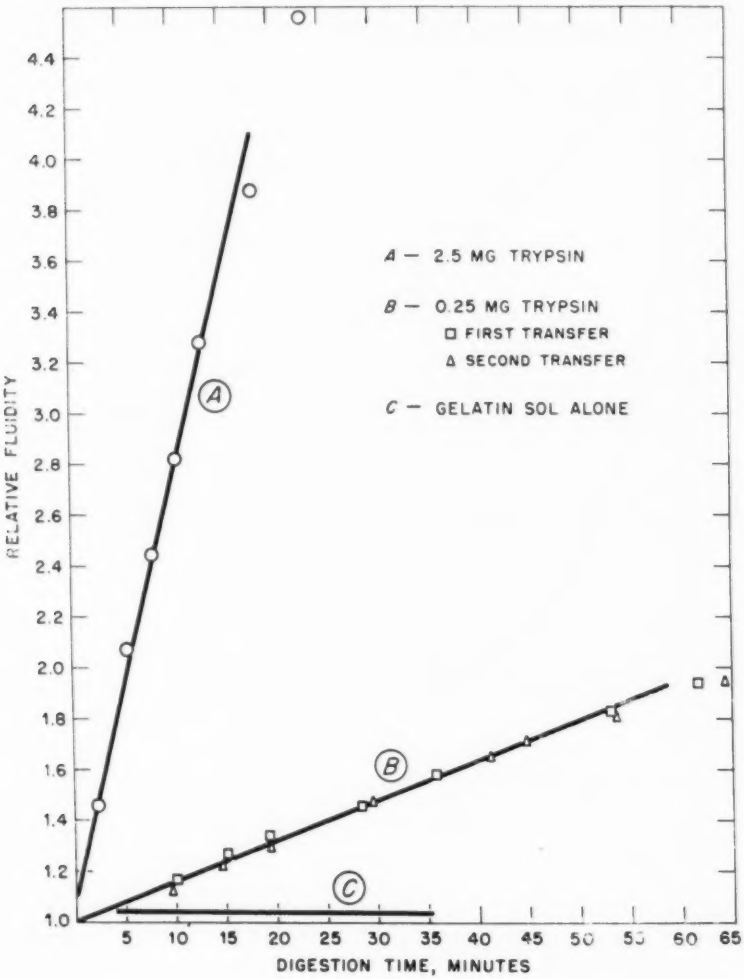


FIGURE 5.

Examination of the conversion graph reveals that efflux times of greater than 100 seconds constitute the best operating range for the viscometer to which it applies. Below 100 seconds larger and larger changes in relative

fluidity arise from small changes in efflux time. That is, as efflux times become short, slight errors in measurement are appreciably magnified.

The determination of proteolytic activity from specific changes in viscosity, as was done for Figure 4, is basically sound but not particularly accurate. Errors of appreciable size can be made, especially in cases of rapid viscosity changes, because the estimate of proteolytic activity is highly dependent on two points in the curve. These two points, in turn, depend upon the goodness of fit achieved when the curve is drawn. As has been mentioned, the preferred fluidity method of making estimates of enzymic activity yields an average of several distinct determinations. Little, if any, error appears to arise from spontaneous hydrolysis of gelatin during the period of enzymes assay.

## Summary

An improved method of determining proteolytic enzyme activity is described. The viscosity of a standard gelatin sol containing enzyme is determined several times in sequence at 5-minute to 10-minute intervals. The observed viscosities are transformed to fluidities by a simple graphical procedure. Fluidities, plotted against time, yield straight lines with slopes proportional to enzymic activity.

Details of method and calculation are given. It is demonstrated that enzyme activity is not lost through combination of enzyme with gelatin split products.

The method can be used in the investigation of bates.

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Acknowledgment is gratefully made to A. C. Lawrence for permission to present this work and to Mr. K. E. Bell for encouragement in the conduct of it.

## Discussion

I. C. Sommerville: I think there are two points which stand out in the results presented in this paper. One is the "fluidity" method of plotting, which gives a straight line instead of the hyperbolic curve. The other is the

evidence offered that the enzyme activity persists for a considerable time, as shown by transplanting where the second sample gives the same hydrolysis on a fresh sample of gelatin as the first.

There is plenty of room for argument as to whether the casein or gelatin method gives the closer approximation to the results obtained in actual bating. There is also a question of how the source of enzyme would affect the relative results with these methods. I do not know if Dr. Holloway can give us any information on these latter points or not.

D. F. Holloway: As to the source of enzyme, we have worked mostly with pancreatic enzymes but also with enzymes of mold origin and found in general that, working with these two types of enzymes, we get good correlation between our results and those obtained from the casein method. We have not worked with bacterial enzymes, but I understand there may be some difference in evaluation.

H. B. Merrill: Did you work with any enzymes which had previously been absorbed on wood fiber or anything of that sort? If so, did you have any trouble eluting the enzyme?

Holloway: We mentioned trypsin here, but a great number of proprietary bates were used and we had no trouble in eluting from the wood fiber.

Merrill: In some work we have done using the calfskin method of Wilson and McLaughlin, we found differences in enzyme activity, depending on whether we added or whether we eluted the bate from the wood meal and filtered the solution. Of course, in the gelatin method it is necessary to elute, because the wood meal would block the capillaries of the viscosimeter. But you experienced no trouble of that sort?

Holloway: No. We do not filter, just let it settle out, and we have had no trouble in checking casein results with this method and relative values between the two different enzymes. There are, of course, salts in the buffered solution used for elution which aid the elution.

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## Use of Polysulfide Liquid Polymers for Impregnation of Leather*

K. R. Cranker and J. S. Jorczak

*Thiokol Corporation*
*Trenton, N. J.*

An interesting and novel development in the application of modified leather products has been accomplished through impregnation of leather with polysulfide liquid polymers [1]. As manufactured and supplied, the liquid polymers

*Presented at the Forty-seventh Annual Meeting, Groton, Conn., June 12, 1951.

are semi-viscous to viscous liquids. The important properties leading to use of these polymers in leather have been based on the ease of impregnation and conversion of the liquids to high molecular weight elastomers. However, the improved serviceability of impregnated leather stems from the unusual aging, oil, and solvent-resistant properties of the elastomers.

The liquid polymers [2] were developed in 1943, and one of the earliest ideas was to investigate the use of these polymers for improving the properties of leather goods. It was soon found that it was possible to fill the voids in leather and then convert the liquid polymer to the rubbery state in place. Studies were carried out on the application of this combination of leather and synthetic rubber for the improvement of water, oil, and abrasion resistance of leather [3].

During the past two or three years the use of liquid polymers in leather has had a healthy growth. Service life of manufactured articles has proven that the original idea is basically sound. The most noted improvements in leather seemed to fit into the mechanical goods field. Although a few tests have been made in shoe and inner soles, uppers and counters, the major activity is still concentrated on applications such as flange seals, pump cups, backup washers, hydraulic packings and cups, and belting.

Three liquid polymers have been found useful in the treatment of leather. All three have the same basic structure with thiol terminals and vary only in average molecular weight. The main repeating segment in the polymeric chain is the formal disulfide unit produced from the interaction of bis-2 chloro ethyl formal and sodiuim disulfide. However, 2 per cent trifunctional agent in the form of trichloro propane is added in the original reaction to develop crosslinks or branch chains along the sides of the main chain. The structure is shown in Table I, and the average properties are shown in Table II.

TABLE I

Basic Liquid Polymer Structure

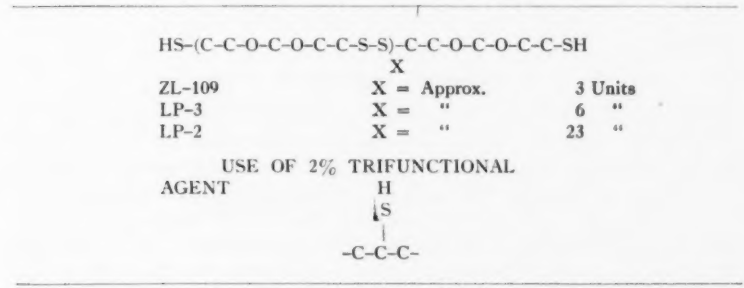

TABLE II

Physical Properties of Liquid Polymers

| | LP-2 | LP-3 | ZL-109 |
|---|---|---|---|
| Approximate Molecular Weight | 4000 | 1000 | 450 |
| Specific Gravity at 25°C. | 1.27 | 1.27 | 1.27 |
| Approximate Viscosity at 25°C (Poises) | 400 | 12 | 5 |
| pH (Water Extract) Range | 6.0–8.0 | 6.0–8.0 | 6.0–8.0 |
| Maximum Water Content | 0.2% | 0.2% | 0.2% |
| Stability at room temperature | over 3 years | over 3 years | over 3 years |
| Color | dark amber | amber | light amber |

## Polymerization Chemistry

The chemistry of the conversion reaction is centered around the reactivity of the thiol terminals and the thiol side chain groups. The most practical procedures used at this time depend on direct oxidation of the thiols to yield a disulfide link with formation of water as a by-product. Since the liquid polymers are manufactured to a very high degree of purity, the polymer formed by this oxidation process attains a very high molecular weight, estimated at 500,000.

Several agents have been found to be successful in converting the liquid polymer in leather. Among these are Cobalt driers, and cumene hydroperoxide. Cobalt acts as a catalyst and makes oxygen in the air available for the conversion process. Cumene hydroperoxide supplies the necessary oxygen with its own structure. Cumene is a good solvent for the liquid polymer so there is no problem of distribution of oxidizer within the impregnated leather. Generally cumene hydroperoxide is activated and stablized by auxiliary alkaline agents such as diphenyl guanidine and triphenyl guanidine.

Some recent tests have pointed toward the possibility of use of reactive resins such as epoxide resins in combination with the liquid polymers. In this case it is believed that the conversion takes place through direct addition rather than by oxidation. Table III shows the oxidation and addition mechanisms.

## Impregnation and Conversion Methods

The cumene hydroperoxide, diphenyl guanidine conversion mechanism is the most universal since it has the least deleterious effect upon commercial leather. However, this procedure is limited to the high molecular weight polymer, LP-2. With the low molecular weight polymers, ZL-109 and LP-3, the conversion with cumene hydroperoxide is very fast and the exothermic reaction causes frothing and gellation of the impregnation bath. Since the LP-2 is quite viscous, it is necessary to thin this polymer with solvents such

TABLE III

Mechanism of Oxidation and Addition Reactions

(1) OXIDATION

$$HS\text{-}R\text{-}S\text{:}H + O + H\text{:}S\text{-}R\text{-}SH$$

(2) ADDITION—epoxide type

$$\text{-C-C-C} + HS\text{-}R\text{-}SH \longrightarrow \text{C-C(OH)-C-S-R-SH}$$

NOTE: R = (C-C-O-C-O-C-C)

as methyl ethyl ketone and toluene. Leather impregnated, using the above process, is limited to applications where complete fill of the leather voids is not required. Conversion of the LP-2 in the leather to the elastomeric state takes place within 24 to 48 hours at room temperature. The treated leather has good flexibility and is low in extractables.

Preimpregnation of leather with cobalt driers followed by impregnation with liquid polymers provides a satisfactory procedure with desirable pH characteristics for fast cure. This procedure gives maximum fill with LP-3 and ZL-109 and very low extractables. This mechanism can be employed with all three polymers. However, it is still necessary to reduce the initial viscosity of LP-2 with solvents. The cobalt cure is not suitable for all leather. The cobalt process has been used successfully on certain oak, vegetable, and chrome tan leather. In many cases all the voids of the leather can be filled, thus making the leather adaptable for high pressure seal applications where a partially filled leather cannot be used.

At the present time, development work is centered around the use of epoxide resins and polysulfide liquid polymers to yield a modified leather having still more desirable characteristics. Through interactions of the resin and liquid polymer in the leather, it is believed that a more tightly knit lattice structure will be obtained. This will offer improved resistance to flow at higher pressures and at the same time cause a substantial improvement in chemical resistance.

Both the cobalt drier and the cumene hydroperoxide processes generally give a fairly flexible product upon conversion of the polymer in the leather. However, for applications requiring leather with a good deal of flexibility, it is possible to introduce chain blocking agents into the liquid polymers thereby limiting the ultimate molecular weight of the polymer chain.

This results in a more flexible end product. Mono-functional mercaptans such as xylyl and benzyl mercaptan can be used as chain blocking agents.

Typical procedures utilizing the cumene hydroperoxide and cobalt conversion mechanisms are shown in Table IV.

TABLE IV

Impregnation Systems
*Leather*

HEXOGEN COBALT 2%) PREIMPREGNATION

1. 10 Min. dip, cobalt solution in toluol.
2. 30 min. drying to allow solvent evaporation
3. 1 Hour drying at 158° F to drive out residual solvent
4. 30 Min. dip in 50% solution of LP-2
   Solvent for LP-2 is M.E.K./toluene 1/1 by volume.

CUMENE HYDROPEROXIDE–TRIPHENYL GUANIDINE CURE

1. 10 Min. in 5% triphenyl guanidine in M.E.K.
2. 30 Mim. drying at room temperature
3. 1 Hour forced drying at 158°F
4. 30 Min. dip in = 50% solution of LP-2
   Solvent is M.E.K./toluene 1/1 by volume
   Cumene hydroperoxide 7
   (Assay. 70%)

## Control of Impregnation

The per cent fill of the voids in the leather can be controlled by polymer solution concentration, and temperature of the impregnation bath.

For controlling the polymer concentration solvents such as methyl ethyl ketone and toluene are used for thinning the polymer. Generally, a 50/50 mixture of the two solvents is more effective than either one alone. Tables V and VI show the effect of polymer solution concentration versus per cent fill of the voids in the leather.

TABLE V

LP-2 POLYMER
Concentration Versus % Fill in Straight Chrome Leather

| LP-2 | Type Cure | % Fill |
|---|---|---|
| 10% | 2% hexogen cobalt | 15 |
| 30% | | 30 |
| 50% | | 32 |
| 70% | | 33 |

NOTE: LP-2 cut with toluene / M.E.K. 1/1

It is noted that maximum fill obtained with use of LP-2 is about 30 per cent. Penetration into the inner voids is prevented by formation of a barrier near the surface. Despite reduced viscosity from thinning, the average chain unit of the polymer has a rather high molecular weight. Rapid oxidation from contact with cobalt increases the molecular weight and reduces motility of the polymer.

TABLE VI
LP-3 POLYMER

Concentration Versus % Fill in Straight Chrome Leather

| LP-3 | Type Cure | % Fill |
|---|---|---|
| 30% | 2% hexogen cobalt | 35 |
| 50% | | 45 |
| 70% | | 75 |
| 100% | | 100 |

NOTE: LP-3 cut with toluene / M.E.K., 1/1

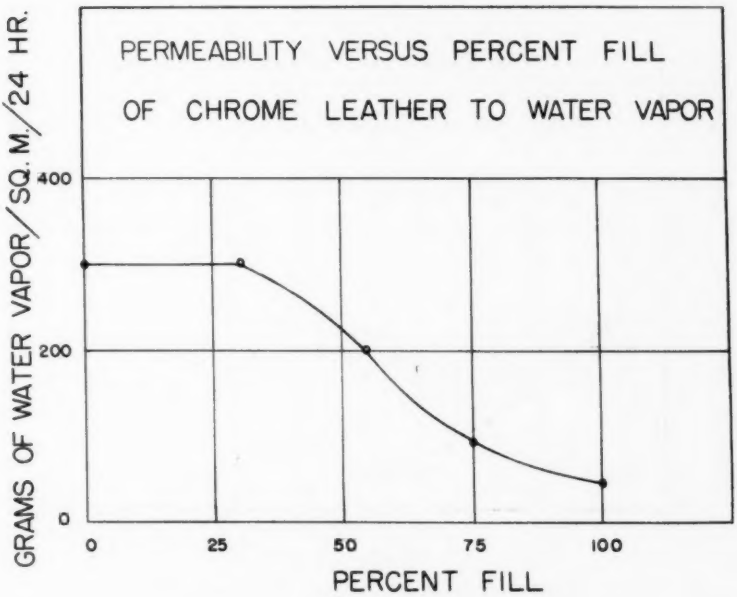


FIGURE 1.

Depending upon the denseness of the leather, the time for impregnation may vary from minutes to several hours. The leather used for hydraulic seals can be impregnated before or after forming the leather to the shape of the seal or cup. When the formed leather is used, the rate of impregnation with polymer is slower. Therefore, immersion has to be carried out over a longer time interval or the temperature of the impregnation bath must be raised. Vegetable tan leather has been impregnated with LP-3 at 150°F. Chrome tan and chrome retan leather have been impregnated at temperatures as high as 180°F without damaging the leather structure. In addition to hastening the rate of impregnation, the elevated temperature is helpful in obtaining maximum fill of the voids.

### Mechanical Properties of Impregnated Leather

Impregnation improves the water and oil resistance of leather. For some uses it upgrades leather and permits use of a less desirable cut or portion in place of top-grade leather. Resistance to penetration of water is roughly proportional to the degree of fill of the voids. It is possible to adjust and control the permeability and to completely stop penetration when all the voids are filled.

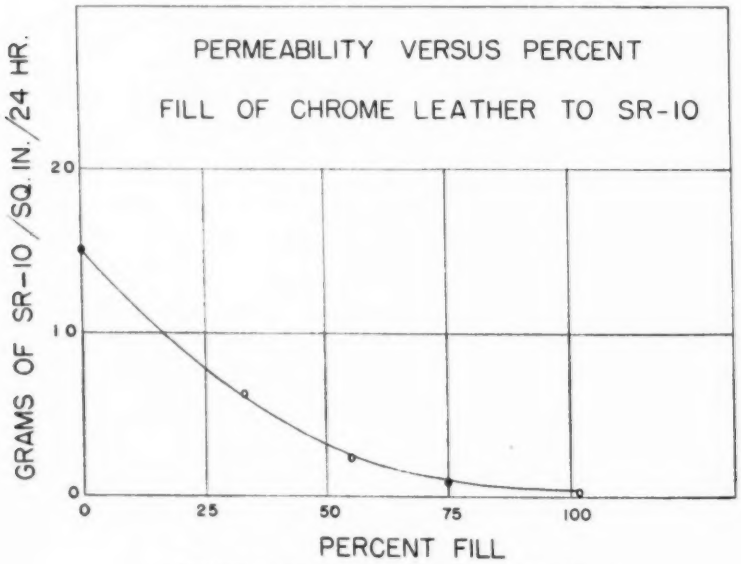


FIGURE 2.—SR-10 IS A.S.T.M. Reference Fuel No. 1. (Diisobutylene)

A much more marked phenomenon is noted when the leather is to be used for preventing passage of gasoline or aromatic fuel blends. It is believed that some swelling of the polymer occurs. In any case very effective reduction in permeability is obtained with partial fill of the voids.

The effect of polymer concentration in reducing permeability to water and gasoline is greatly dependent on the type of leather used and possibly the

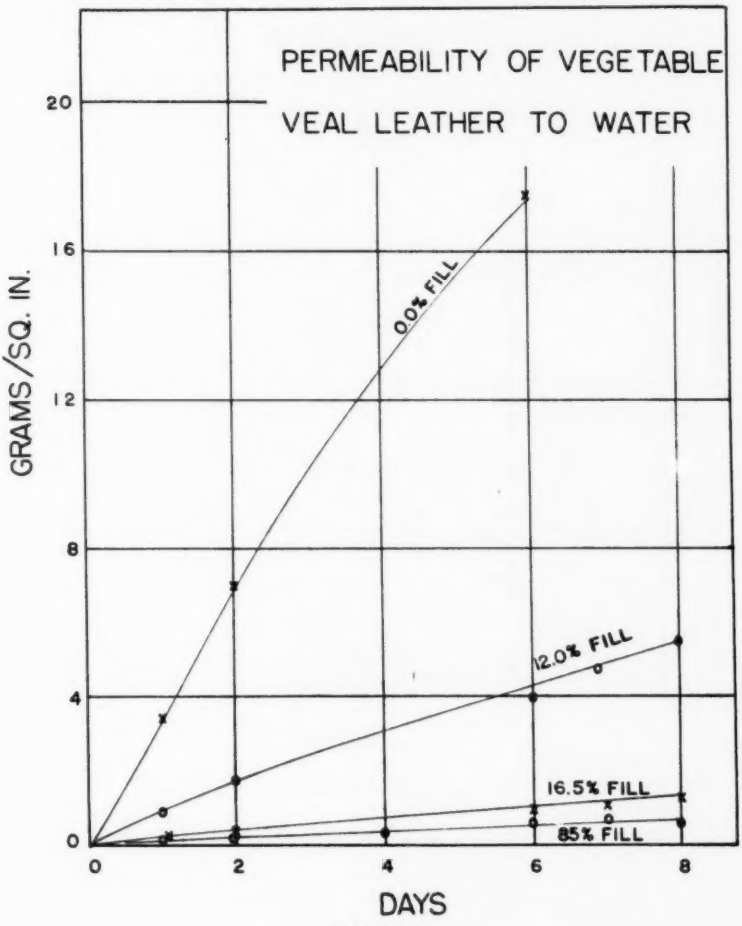


FIGURE 3.

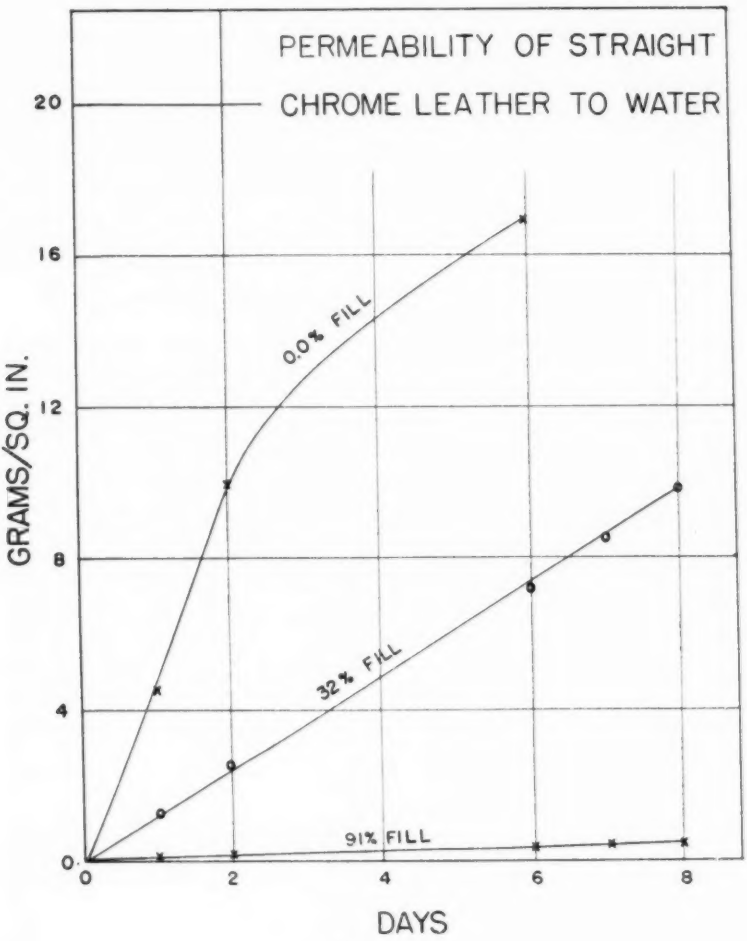


FIGURE 4.

tanning treatment. For example, water penetration was effectively stopped in vegetable veal leather with a fill of 16.5 per cent; whereas straight chrome tanned leather required 90 per cent fill to reach a similar state*

*Fill is that percentage of the leather voids in which the polymer has penetrated.

The effect of impregnation in reducing permeability of water in midsole leather is shown in Figure 5. The voids in this leather were considerably less than those observed in the other samples tested.

Once the liquid polymer has formed into the elastomeric state, it is permanently locked in place. It cannot be dissolved by most solvents and can only be removed by chemical destruction.

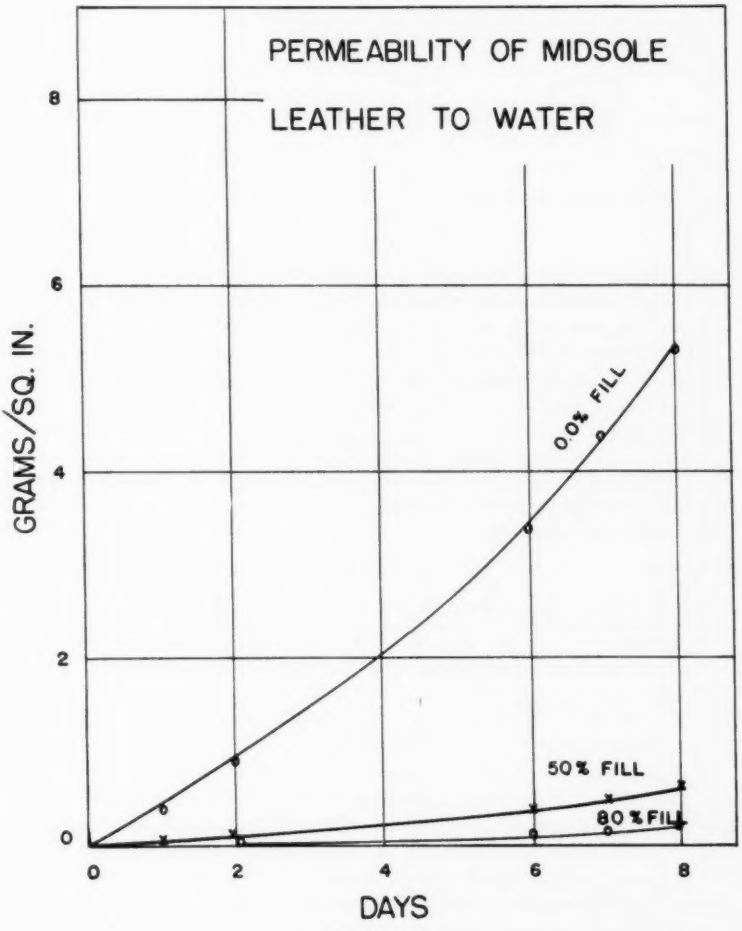


FIGURE 5.

Chloroform and water extractions have been run following procedures A.S.T.M. D297-43T and D814-46T. Values observed are low and show very little difference when increasing amounts of polymer are deposited in the leather.

TABLE VII

Chrome Leather

| % Fill (LP-2)* | % Chloroform Extract | % Water Extract | pH |
|---|---|---|---|
| 0 | 5.4 | 1.5 | 3.3 |
| 10% | 6.0 | 1.4 | 4.2 |
| 30% | 7.2 | 1.7 | 4.5 |
| 50% | 8.0 | 1.9 | 4.9 |
| 70% | 8.0 | 1.5 | 4.7 |

*Cumene hydroperoxide conversion

## Summary

A simple and useful way of filling leather with liquid synthetic rubber has been developed. Practical applications have been established in leather mechanical goods. The change in mechanical properties has overcome some of the limitations of leather and has improved the position of leather use for applications such as oil seals. The combined properties of leather and elastomer are better for some uses than either leather or synthetic rubber.

## Acknowledgment

The authors are indebted to the laboratory staffs of the Development and Technical Service Departments, who obtained much of the information upon which this article is based.

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3. R. Oehler and T. J. Kilduff, *Research Nat'l Bur. Standards*, **42**, 63, (1949).

Received June 14, 1951

## Discussion

R. Oehler: Several papers presented here today have demonstrated the wide interest in the application of polymers to leather, both as resin tannages and as impregnants for tanned leather. Polymers may be introduced as emulsions, by means of solvents, or they may be formed within the leather itself.

The paper presented by Mr. Cranker shows a skillful combination of solvent impregnation followed by polymerization *in situ*. It demonstrates that certain properties of leather may be modified for specialty uses. The process has con-

siderable flexibility, is subject to close control, and has been used commercially for several years.

Many of us would like to see the development of a method for impregnating with polymer emulsion. In this connection Dr. N. D. Cheronis has developed several emulsions, employing acrylates, silicons, and Thiokols for treating chrome tanned horse fronts to be used as glove leather.

Now, I have two questions for Mr. Cranker.

First, in a commercial application, are the solvents removed by forced drying generally recovered, and second, if the solvent removal was carried out about 80°C could the cumene hydroperoxide cure be made without guanidine, and how much time would be required?

CRANKER: In answer to the first question about the solvent removal, actually customers of ours could answer that question better than I. However, I do believe there are no existing facilities for solvent recovery because of the economy of the situation. It is cheaper just to discard the solvents that are in the polymer. I may be wrong. If so, some one can correct me. Because I do not know what procedure every company has.

The second question about cumene hydroperoxide, if this converted impregnated leather is used at elevated temperature, we believe the converting mechanism with cumene alone is not practical since the cumene hydroperoxide will decompose with time to form acids and acids will revert the liquid polymers. For safety we applied a buffering medium such as triphenyl or diphenyl guanidine.

For most applications at room temperature, the cumene alone would be suitable. However, we believe that the proper pH conditions for leather and rubber are presented when the buffering system is utilized. Also, the cumene conversion is generally too slow for practical use unless D.P.G. is used as a booster.

SHU-TUNG TU: About the recovery of solvents, can we use water emulsion first?

CRANKER: You are getting into some one else's field. There are some people now actively engaged in that; at Thiokol, we have not started any program, because of pressing business. However, we do know that some encouraging results have been obtained by obtaining the right charge upon the emulsion deposit in the leather causing the emulsion to break leaving polymer *in situ*. That is all I know, unless someone might be able to supply additional information.

J. R. KANAGY: How do you determine the percentage of fill?

CRANKER: At our laboratories we use the word "pickup," which is, for instance, if the leather weighs 10 grams before it is impregnated, and after impregnation 20 grams, that means it picks up ten grams or one hundred per cent by weight. For straight chrome leather, a 100 pickup was roughly 100 fill of voids, for vegetable leather, 75 per cent pickup was roughly 100 per

cent fill of voids, and for midsole leather a 30 per cent pickup was a 100 per cent fill of voids.

KANAGY: Do you actually fill the voids?

CRANKER: We impregnate with methyl ethyl ketone and right afterward obtain the weight of methyl ketone that went into the leather and by ratios of the specific gravities of the polymer and ketone we determine the approximate fill we could get with the liquid polymers. We assume maximum fill of the voids with the ketone.

The idea is rather confusing because in lots of cases there are going to be films formed over the surface and usually one may interpret that—there is not uniform impregnation but just a film over the surface. We do not report data on leather which we feel has had a barrier formed on its surface for we cut all impregnated test pieces in order to examine them for through impregnation. A barrier is often formed with the cobalt process and that is why I said it cannot be used for all leather.

NOTE: (There was another question asked me, Mr. Cranker, about solvents used for cutting or thinning the polymers).

CRANKER: We recommend just from our laboratory experiments using methyl ketone and toluene. Some customers use ethlene dichloride to cut the polymers. It volatilizes off rapidly and results in quick drying.

F. D. THAYER: You mentioned you use synthetic polymers for impregnating leather belting. Could you tell us the advantages that are gained through this use?

CRANKER: Most of our commercial applications or most of the polymer sold is in the oil-seal field. We have done a small amount of work on aprons and belting for other companies. I cannot say too much about that at the moment, but it has improved working life of the belts (based on the rough tests made in the textile mills) we will say, from 100 to approximately 350 to 400 hours in actual test operation.

Some one in the audience might know more about what those aprons are used for in the textile field.

MR. LONG: In the formation of these packings, how long do you have to keep the leather in the mold before you can remove and retain the set? Do you have any problem of flaring afterward?

CRANKER: I cannot say, because that is what our customers do. Some one in the audience might be able to answer that. We don't do any forming of leather. I made that statement in my paper, because I know that some of our customers impregnate before or after forming of the cup. How long it takes, I cannot tell you.

H. D. SENTKOWSKI: Once the leather is cured for 24 hours, you can mold it at a temperature of 307°F for about one minute.

LONG: You can chill immediately at exact diameter, because if you do not, there might be separation afterward caused by taking up moisture.

A. N. KAY: I have a couple of questions. The one I think Dr. Kanagy mentioned was this question of film formation, dipping the way you do. How would you remove the film from the surface so that you leave the appearance of a leather surface rather than a polymer surface?

CRANKER: In the laboratory, all we do is wipe it off with some sort of paper towel or cloth. I guess in real commercial applications there are regular squeeze rolls where the leather is passed through at a fairly open setting. Others may be able to verify that. But they have a definite setup. Each one has a different wiping operation.

KAY: I should also like to ask about adjusting the concentration and viscosities of the polymers. I was wondering whether different polymers were used because of the color of the finished product.

CRANKER: To answer your question about the use of different polymers, we only use different polymers in order to vary the percentage fill of polymer in the leather. The low molecular weight polymers are used because they are very slightly viscous and are used where a higher fill of the voids is needed. LP-3 and ZL-109 are the low viscosity polymers used without solvent thinning.

The color of finished polymer does not vary too much, and does not affect the color of the converted or cured impregnated product. I have several samples of impregnated hydraulic packings, and they are all of the same color, namely a brown-black color.

In the cure there probably is a sulfide formed which causes a blackening. It does not seem to hurt the leather.

In most all cases the impregnated leather has a darker color.

KAY: My other question concerned the permeability test. How was that carried out?

CRANKER: It was carried according to the ASTM procedure. We took a two inch died out disc positioned properly in a Thwing Cup which was inverted. A weight reading was checked daily.

J. MALIK: Does high grease interfere with this treatment procedure or grease compatibility with the polymer?

CRANKER: That is a good point. In the impregnation process we degrease any leather which has a grease content above 6 per cent, because it is hard to obtain an accurate estimation of the void fill if grease is present. That is our thumb rule in the laboratory. Some places may degrease if the content is above 3 or 4. But we degrease when it is above 6.

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## ABSTRACTS

**Notes on a Modified Kjeldahl Apparatus.** By K. A. Hyde, *Chem. and Industry*, No. 50, 1103 (1951). The author describes a modified Kjeldahl apparatus for use in small laboratories where a limited number of protein determinations are carried out. The digestion

apparatus consists essentially of a Kjeldahl flask connected in a train of two gas washing bottles, the latter of which is connected to a vacuum pump. The first bottle contains water and the second caustic soda. The tube connecting the Kjeldahl flask with the first gas washing bottle is provided with a vent to prevent the development of low pressure in the digestion flask. A suitable distillation apparatus is also described and illustrated.

**A New Generator for Hydrogen Sulfide and Other Gases.** By J. F. D. Marsh, *Chem. and Industry*, No. 51, 1134 (1951). A new generator for hydrogen sulfide and other gases has been devised for the production of a constant but adjustable gas pressure. The gas is produced by the admixture of two liquids, and its output is dependent on the flow of only one of the two reagents. The gas supply does not need to be interrupted when replenishing the reagents.

**Effect of Digestion Temperature on Kjeldahl Analyses.** By G. R. Lake, P. McCutchan, R. VanMeter and J. Neel. *Anal. Chem.*, **23,** 1634 (1951). Temperature of digestion of sample was found to be of prime importance. Too low a temperature requires too long a digestion period or fails to give good results while too high a temperature may result in a loss of nitrogen. Temperature or digestion is regulated by the amount of potassium sulfate in the digestion mixture.

**Quantitative Paper Chromatography of Amino Acids.** By A. R. Patton and P. Chism. *Anal. Chem.*, **23,** 1683 (1951). Some of the variable factors involved in this technique were evaluated, with the object of establishing the quantitative reliability of some published techniques, and of improving their reliability where indicated. When scanned through the vertical axis (direction of flow), the amount of an amino acid after separation on paper by chromatography and reaction with ninhydrin is quantitatively related to optical transmittance density. The amount of a given amino acid is determined by locating its $R_f$ density curve area on a standard area-concentration curve previously plotted for the same amino acid, or, under suitable conditions, by locating its maximal density on a similar standard density-concentration curve. Successive chromatograms are equilibrated by constant application of a known amino acid solution. Time-density curves indicate better results with ninhydrin dissolved in ethanol rather than the customary butanol, and color development in the dark at room temperature not less than 18 hours after spraying. Published methods are extended, including description of procedures in greater detail, more thorough exploration of certain variables in technique, and introduction of new techniques.

**Determination of the Particle Size of Fine Powders, with Particular Reference to Kaolins.** By C. Rossie and R. Baldacci. *J. Applied Chem.*, **1,** 446 (1951). The sedimentation curves for suspension of kaolins from Central Europe, Italian bentonites and clays have been obtained by using a hydrostatic balance provided with a normal plunger. Investigations undertaken to establish the accuracy of the method and the theoretical calculation of the sedimentation curves are briefly described. The possibility of applying Stokes law to the mass settling of kaolins is also discussed. The authors wish to emphasize (a) the possibility of determining the average diameter of powder particles by means of the tangent to the curve at zero time, and (b) the possibility of deducing from experimental sedimentation curves, both the curves relating to size distribution (the number of particles as a function of equivalent diameter) and the cumulative curves (the percentage by weight of particles having dimensions smaller than one determined equivalent diameter). When carrying

out sedimentation measurements, particularly with kaolins, it is possible to obtain regular curves only when conditions are such as to avoid flocculation. This result is achieved by adding suitable electrolytes in quantities which determine the smallest sedimentation volume. The average equivalent diameters of the powders examined were deduced from such sedimentation curves. Statistical measurements of dimensions made by direct microscopic observations have been carried out on two kaolins from Central Europe, resulting in average values which agree very closely with those calculated from the sedimentation curves. Cumulative curves of the usual type have been obtained from the densimetric curves of sedimentation.

**Automatic Distilling Apparatus for Continuous Production of Conductivity Water.** By R. C. Bieber and N. Ibl. *J. Applied Chem.*, **1**, 503 (1951). A simple laboratory device is described which allows the double distillation of water in a continuous and automatic way in order to produce particularly pure water. The water thus obtained has a mean specific conductivity of $0.5 \times 10^{-6}$ ohm$^{-1}$ cm.$^{-1}$ at 25°C. It is an electrically heated glass still which has proved reliable in action for several years and is able to run for several days without attention. The first distillation is carried out in the presence of potassium permanganate and sulfuric acid to oxidize organic impurities. To remove carbon dioxide the condensed vapors of the first distillation are continuously saturated with solid barium hydroxide while flowing to the second still. Reliable automatic working of the still requires devices (a) to keep the water level in both flasks constant, and (b) to protect the apparatus from breakage by switching off the whole power supply in case of accidental interruption of the feed-water supply to either flask. This is realized by controls worked by two floats which are placed in small communicating side-vessels. Each float is provided with a mercury-containing glass tube open at the upper end. Contact-wires dip into the mercury. They are attached to plugs on insulated, movable electrode-holders, and lead through insulated brass tubes serving as guides to the floats.

**The Determination of Total Sulfur in Coal. Comparison of Eschka and Strambi Methods.** By I. Davies and P. J. Jackson. *J. Applied Chem.*, **1**, S4 (1951). The Eschka and Strambi methods of determining the total sulphur content of coal have been compared in a series of determinations on coals of widely varying sulfur content. A serious discrepancy has been found between the two methods; this has been traced to one point of technique in the Strambi method. A modification has been made to the Strambi method which enables it to give results in agreement with the Eschka method.

**The Measurement of Particle Size Distribution by Sedimentation Methods.** By E. H. Amstein and B. A. Scott. *J. Applied Chem.*, **1**, S10 (1951). The results in this paper are confined to the pipette method of sampling a suspension. The importance of dispersion is stressed, and tests are described for the determination of the adequacy of dispersion, based on microscopic examination, observation of rheological behaviour, and qualitative and quantitative sedimentation. The effect of partial flocculation on the sedimentation results is demonstrated. It is shown, however, that provided dispersion is complete, a 16-fold change in the concentration of solids has no detectable influence on the results up to a concentration of 2 per cent by volume. This result was obtained on calcined alumina, but some examples are also given of work on hydrated alumina and carbon powders. In the case of coke powders the results of sieving and sedimentation are in good agreement. The methods of presenting these results are discussed, and it is considered that the cumulative undersize by weight on a logarithmic basis is the form most generally useful.

**Organic Adsorbents from Indian Tannins. I. Preparation, Activation and Relative Adsorptive Power.** By M. S. Bhatnagar and P. C. Nigam. *J. Applied Chem.*, **1,** 517 (1951). Many workers have described costly phenol-formaldehyde or amine-formaldehyde resins for ion-exchange. Tannins of the catechol type can also be used for the same purpose. In a previously published communication (Bhatnagar & Singh, 1950), it has been shown that katha (the edible material used in betel leaves) yields on sulfonation products which exhibit calcium and magnesium exchange. More resins from katha and cutch have now been prepared and their adsorptive properties have been studied. The products obtained by sulfonation of katha and cutch and subsequent condensation with formalin are found to adsorb about 95 per cent and 65 per cent fatty acids respectively from centimolar solutions. The resins obtained by mere sulfonation show little adsorption of acids. The products obtained by direct condensation of katha and cutch with formalin exhibit 15 per cent and 6 per cent adsorption respectively of benzoic acid. On the other hand, resinous products obtained by incorporation of katha and cutch in phenolic resins prepared using ammonia as a catalyst show high adsorption values, namely: 55 per cent and 70 per cent respectively of benzoic acid and formic acid. The adsorptive properties of standard resins, e.g., Amberlites, Zeo-karbs, etc., have also been studied. The study reveals that the prepared resins are comparable with standard resins.

**Organic Adsorbents from Indian Tannins. II. Adsorption of Acids, Bases and Salts.** By M. S. Bhatnagar and P. C. Nigam. *J. Applied Chem.*, **1,** 520 (1951). The adsorption of homologous series of monobasic and dibasic aliphatic acids by katha and cutch resins has been studied. The adsorption decreases with the increase in the molecular weight. This reversal of Traube's rule is explained on the basis of orientation of molecules at the resin-water surface according to the theory of Langmuir and Harkins. The influence of substituted hydroxyl groups has also been studied. The adsorption of barium, strontium and calcium has been studied. The order of adsorption is explained on the basis of the polar concept.

**Extraction of the Active Agent from Detergent Mixtures.** By S. A. Miller, B. Baun and A. P. Ponsford. *J. Applied Chem.*, **1,** 523 (1951). It has been found that *n*-butanol can be used to extract the active agent quantitatively from dilute solutions (0.4–4.0 per cent) of a great variety of surface-active agents. In order to obviate hydrolysis in some cases it is necessary to add sodium sulfate or carbonate and, as a routine measure, 4 per cent of sodium carbonate (on the aqueous solution) can be added in all cases. The butanol extract can then be evaporated *in vacuo* and weighing the residue. Extractions were carried out in Kieselbach extractors for 3 hours using 250–1000 ml. of dilute solution. The amounts of active agent in aliquots of the original aqueous solutions and the butanol extracts were determined by the method of Epton as regards anionic and cationic detergents. With nonionic detergent, the concentration of active agent in the original solution was estimated by evaporation of a sample and extraction of the dry material with ethanol. Butanol extraction on a 16 different detergents showed an efficiency of about 80 per cent. The completeness of the hydrolysis in absence of carbonate appears to be a characteristic of secondary alkyl sulfates and may constitute a ready means of distinguishing them from primary alkyl sulfates, which are partly extractable under these conditions.

**Determination of Moisture by Distillation.** By W. R. Fetzer. *Anal. Chem.*, **23,** 1062 (1951). The author reviews the numerous applications of the distillation procedure

for moisture, and illustrates about 17 designs in apparatus which will adapt the procedure to a specific product. The distillation procedure for moisture determination is applicable to materials which cannot be analyzed or give questionable results in the usual oven procedure. It should not be used when the oven method can be used.

**Small Scale Filter Paper Chromatography.** By L. B. Rockland, J. L. Blatt and M. S. Dunn. *Anal. Chem.*, **22,** 1142 (1951). Because of the growing interest and importance of filter paper chromatography as a tool for the qualitative identification and quantitative determination of amino acids and other biological substances, investigations were conducted on thirteen filter papers, and these rated on the basis of seven physical and chemical characteristics. These characteristics were texture, solvent boundary, uniformity, area weight, solvent speed, ninhydrin color and resolving power. The influence of the paper on the $R_f$ values of 18 amino acids was studied, the influence of water content of 8 water-miscible solvents on $R_f$ values of amino acids was investigated, and the $R_f$ values (ratio of the length of the chromatogram to the distance traveled by the solvent boundary) of amino acids representative of the acidic, basic, neutral, and cyclic groups were determined. The fixed and most common sequences of the amino acids, the solvents yielding inverted sequences, and the solvents most effective in separating individual amino acids, pairs of amino acids, and groups of amino acids were determined.

**Acidic Behavior of Concentrated Boric Acid Solutions.** By D. W. Stetten, Jr., *Anal. Chem.*, **23,** 1177 (1951). The author noted that after significant quantities of ammonia vapor were delivered into 4 per cent aqueous boric acid containing methyl red-methylene blue indicator, the expected change in color (purple-green) did not occur until after the mixture had been diluted with distilled water. Only after considerable dilution had been effected could the ammonia be satisfactorily titrated with hydrochloric acid. This led to an investigation of the matter with the observation that in concentrated boric acid solution as much as 0.005 equivalent of alkali may be required to bring the acid to the turning point of the indicator. This quality falls off rapidly as the solution is diluted, and virtually disappears when the concentration falls to 0.1 *M* or below. In the Kjeldahl procedure for nitrogen the recommended quantity of boric acid is in enormous excess, often 50 to 100 fold the amount of ammonia collected, on a molar basis. As usually conducted, the Kjeldahl distillation effects sufficient dilution of the boric acid to minimize the error which would otherwise result.

**Continuous Weighing in Analytical Chemistry.** By C. Duval, *Anal. Chem.*, **23,** 1271 (1951). By registering photographically or by pen, the curve representing the loss or gain in weight undergone by a heated substance, important facts are brought to light, which are not revealed by the classic method of discontinuous weighing. In this way it is possible to determine gravimetrically many materials, either alone or in mixture, by an automatic process which involves no personal error in weighing. The new method lends itself to numerous determinations of humidity and ash. The greatest advance realized through the thermobalance is the fixing of the exact limits of temperature between which a given precipitate acquires a constant weight, a condition indispensable to the making of a sure weighing.

**Linear Starch Reagents.** By J. L. Lambert. *Anal. Chem.*, **23,** 1247 (1951). The cadmium iodide-linear starch reagent had been reported in two previous papers by the author and coworkers, but no extensive study made of the reagent itself. This work was primarily intended to study the reagent more thoroughly and to point out its usefulness and potentialities for the colorimetric determination of trace amounts of oxidizing substances. The intensity of the starch-iodide blue color developed in solution was found to be directly pro-

portional to the concentration of the oxidizing agent over relatively wide ranges. Rate of color development was studied and the extinction coefficient determined. The reagent is colorless, unaffected by age, and capable of giving highly reproducible results. This reagent makes possible the first satisfactory utilization of the extremely delicate starch-iodine reaction for colorimetric work, and has the added convenience of stability. It should make possible the development of a number of new analytical procedures.

**Linear Starch Reagents.** By J. L. Lambert. *Anal. Chem.*, **23,** 1251 (1951). This study was made on a colorimetric reagent containing linear A-fraction potato starch, iodate ion, and cadmium ion which, at the proper pH, indicated a selectivity for iodide ion. The colorless reagent so prepared proved to be stable for periods up to 6 weeks and to be selective for iodide ion when used in a solution of a weak acid such as formic. The reaction of iodate ion and iodide ion to produce tri-iodide ion ($I_3$), which reacts with the linear starch to form the well-known blue complex, gives reproducible and quantitative results. Very few substances were found to interfere under such conditions. The rate of color development and the effect of temperature were studied, and the extinction coefficient was calculated. This reagent makes possible the selective colorimetric determination of iodide ion in very dilute solution. Analytical procedures for very small amounts of iodide ion are of current interest in such fields as medicinal chemistry and water purification.

**Determination of Oxygen-Consumed Values of Organic Wastes.** By W. A. Moore, F. J. Ludzack and C. C. Ruchhoft. *Anal. Chem.*, **23,** 1297 (1951). The shortcomings of the permanganate method for the determination of oxygen consumed in stream sanitation and industrial waste studies led to the proposal of several other methods during the past few years. In order to evaluate the proposed methods a comparative study was made of them. It was found that when silver sulfate was used as a catalyst in conjunction with the Moore procedure, higher oxidation values were obtained than with the other methods studied. Statistical evaluation of the data indicated that the Moore acid dichromate method is applicable to a larger variety of wastes with advantages in precision and reproducibility. It also has advantages in ease of manipulation and time required.

**Fuchsin-Sulfite Reagent in Colorimetric Determination of Formaldehyde.** By L. Segal. *Anal. Chem.*, **23,** 1499 (1951). When the reagent was prepared from basic fuchsin (rosaniline hydrochloride) according to standard procedure, appreciable color varying from tan to red was found to remain after the addition of the hydrochloric acid. This color was removed by shaking with a decolorizing carbon, after which concordant results were obtainable. The author cautions against the use of excessive amounts of decolorizing carbon since this will result in complete loss of sensitivity of the reagent, that is, no color will develop in the presence of formaldehyde.

**Determination of Acid Number of Oils and Resins in Aqueous Medium.** By G. Narsimhan and S. A. Saletore. *Anal. Chem.*, **23,** 1315 (1951). In the customary determination of the acid number of oils, the object of the alcoholic titration is to prevent the soap formed from undergoing hydrolysis and giving rise to a premature end point. The titration could be carried out in aqueous medium provided the hydrolyzing tendency of the soap is either eliminated or kept at a minimum. The authors accomplish this by emulsifying the sample and titrating the dilute unstabilized emulsion with aqueous alkali. Turpentine is used as solvent for the oils or fatty acids, to be mixed with neutral alcohol. Titration is with alcoholic potash and the end point is determined with indicator or potentiometer.

**Structure of Collagen. I. X-Ray Investigation of the Denaturation of Collagen.** By B. A. Wright and N. M. Wiederhorn. *J. Polymer Science*, **7**, 105 (1951). Through *J. Soc. Dyers and Colourists*, **67**, 482 (1951). Collagen shows a low-angle X-ray diffraction pattern corresponding to a spacing of ca.650 Å. On denaturation (shrinking) this pattern vanishes and does not return, regardless of subsequent treatments. When collagen tendons are stretched taut in water above the shrink temperature, the intensity of the low-angle pattern appreciably diminishes. This is due to decrease in concentration of the structure which gives rise to the pattern, and indicates melting of the crystalline structure of collagen. At constant temperature (above the shrink temperature) the low-angle pattern continually decreases in intensity with increased shrinkage until it disappears completely. The extent to which shrinkage must occur before the pattern disappears depends upon temperature and increases with decreasing temperature. The heat and entropsy of shrinkage indicate that the fusion is a stepwise process involving very few amino acid residues in each step (perhaps only one or two residues). The heat and entropy of shrinkage apparently decrease with increasing tendency toward swelling. Thus the heat of shrinkage for formaldehyde tanned is greater than for untanned collagen, and the heat of shrinkage for native collagen is greater in water than in formamide.

**The Determination of Magnesium Sulphate In Leather.** By T. I. Pound. *J. Soc. Leather Trades Chemists*, **35**, 191 (1951). The official method for determination of magnesium sulfate in vegetable tanned leathers is lengthy and unsuited to rapid routine work. This method is put forward as an alternative to the previously published Spiers method. It is based upon removal of Fe, Al and Zn by NaOH at pH 8.0 to 8.5 and then the titration of an excess of known alkali, which has been used to precipitate the magnesium as hydrate, under conditions which give a quantitative result with a sharp end point. Specifically the method is as follows. The ash from 5-10 grams of leather is moistened with 0.2 *N*HCl added in the presence of thymol blue until a pink color is obtained. Boil to remove carbon dioxide, cool to room temperature and add 0.2 *N*NaOH ($CO_2$ free to a greenish blue color. Rinse into a 25 or 50 ml. flask, bring to volume and filter. To an aliquot portion (e.g., 10 ml.) add 5 or 10 ml. of 0.2 *N*NaOH, shake; add 10-20 drops of thymol blue and 2-3 times the total volume of acetone. Then titrate with 0.2 *N*HCl until the blue color changes to greenish yellow. One ml. of 0.2 *N* NaOH = 0.0246 gr. $MgSO_4 7H_2O$. The NaOH must be $CO_2$ free. it may be made by treatment of the alkali with 1-2 gr. of barium chloride per liter and using the clear supernatant solution. The acetone should be freshly distilled over a little alkali. Fifty ml. of the acetone plus 5 ml. of water plus thymol blue should give a blue color with one drop of 0.2 *N*NaOH. Full blue color should be reached in the precipitation of the Al. Keep volume small for final titration. It is best to standardize the reagents against a known solution of magnesium. See the following report of the analyses committee for comments on the method. R. H. T.

**Leather Analyses Committee-Progress Report No. 2.** By G. Forsyth. *J. Soc. Leather Trades Chemists*, **35**, 193 (1951). A comparison of the Spiers method with the Pound method for determination of magnesium sulfate shows the following. Sensitivity: Spiers method variable, Pound method 0.001–0.002 gr. magnesium sulfate. Both show reasonable agreement with the Official Method. Time for analysis: Official Method, 24 hours; Spiers, 1-2 hours; Pound, 0.5-1 hour. Color changes: Spiers method occasionally indefinite, Pound method definite. Spiers method requires experience and special reagents. Pound method requires no particular skill and ordinary reagents. The committee concludes that both methods give reasonable results, but recommends the Pound method if highly skilled technicians are not available. R. H. T.

**Unsulfited Quebracho in the Hot-Pitting and Drumming of Sole Leather and Its Effect on Water Resistance Under Static Conditions.** By G. H. W. Humphreys. *J. Soc. Leather Trades Chemists*, **35,** 193 (1951). It is generally believed that the incorporation of quantities of unsulfited quebracho in the hot-pitting or warm drumming process at the end of sole leather tannage will increase resistance of the finished leather to the uptake of water, but no actual figures have been available to support the conclusion. The effect is considered to be due to inducing the insolubles, or difficult soluble tannins, into the leather while warm. An experiment to check these contentions was made in which tanned but unfinished leather was hot-pitted in liquors made up of unsulfited quebracho and mimosa extract in varying amounts. The pieces of leather were finished normally but with care to see that all received exactly similar treatment. The resultant leather was tested for $Q_{15}$ (initial uptake of water in fifteen minutes), $Q_{24}$ (water uptake in 24 hours), water resistance (Edwards Apparatus), free water and degree of tannage. The figures showed decreasing values for $Q_{15}$, $Q_{24}$ and free water, increased water resistance under static conditions and a progressive increase in the degree of tannage. The work was confined to hot-pitting but it was felt that even better results might be obtained by warm drumming. R. H. T.

**Variations With pH of the Tensile Properties of Collagen Fibers.** By R. H. Hall. *J. Soc. Leather Trades Chemists*, **35,** 195 (1951). The experiments described consist of carrying out load compared to extension tests on collagen fibers immersed in liquids. The fibers used were acetone dried ox cheek and were tested in water at almost the full range of pH. A new apparatus was used so constructed that the extension corresponding to definite loads could be noted without changing to look at the load scale directly. Correction of drift, due to warping of the table top, was made. The extension of the fiber was measured by the optical lever method. A simple micro-balance for weighing the fibers is described. The work required to stretch the fibers, plotted against pH, showed a small drop from pH 1 to 2. There was then an almost vertical rise, between 2 and 3, to the maximum work. This maximum was maintained, with a slight falling off, up to pH 11. Between 11 and 12 there was an almost perpendicular drop back to the same value (minimum value) as at pH 2. A curve plotting the water uptake against pH is roughly a mirror image of the above described curve. When the work of extension is low, the fiber apparently swells and takes up water. It was found that the fibers came to equilibrium with the liquid in which they were immersed in 24 hours. Only at the highest pH (12.9) was there any appreciable damage to the fibers in 24 hours. Values for Young's modulus for six fibers, taken at pH 7, vary from 0.70 to 2.09 measured in $10^{10}$ dynes per cm.$^2$. Density, in grams per cc. varied from 0.929 to 1.296. The large variation in density may be due to air space. When the values of Young's modulus were plotted against cross sectional areas of the fibers, it was found that fibers of small cross section gave the highest values of the modulus. No explanation for this phenomenon is known. The mathematical interpretation of curves is given and various theoretical formulae, relating load and extension, are compared with the experimental results. It is considered that further work, now in progress, is needed to establish the relative importance of entropy and internal energy effects in the elasticity of collagen fibers. R. H. T.

**The Chromatographic Examination of Tannin Extracts.** By W. E. Hillis. *J. Soc. Leather Trades Chemists*, **35,** 211 (1951). In view of the success of paper partition chromatography in various fields it seemed the technique could be applied to examination of tannins. Samples of cube gambier, Indian cutch, quebracho, wattle, myrabolam, "Myrtan" and solution extracts of brown mallet bark and Dundas mahogany were used for study. The resolving solvent mixtures were: butanol: acetic acid: water as 40:10:50; m-cresol: acetic acid: water as 50:2:48 and phenol: $_2N$ hydrochloric and acetic acids as 50:50. The most chromogenic spraying agent tried was Tollen's reagent. A Mercra 125 W., M.B.W. 49,

ultra-violet lamp with ultra-violet filter was used for examination. Patterns of the chromatograms produced are given with a key giving the color, fluorescence, intensity, etc. A fair degree of success in resolving the tannins was obtained. The most distinctive feature was that cube gambier, cutch, quebracho and wattle contain many components having a yellow fluorescence under ultra-violet light, while the remainder of the samples have a predominately mauve fluorescence. This indicates that the yellow fluorescence is given by members of the flavo tannin type while the gallotannins give a mauve-white fluorescence. Three different shipments of wattle and myrobalam were examined and all three gave identical chromatograms in both cases. Therefore, chemically at least, they may be considered uniform. This limited survey shows that the technique has promise as a means of rapidly assessing the nature of vegetable tannins. Observations of White, who showed that quebracho tannin is a complex mixture, have been confirmed; and the complexity of the other tannins examined is also evident. The results of this work do not confirm numerous current theories which suggest that tannins consist mainly of a large polymeric substance or a series of related polymers based on the catechin unit. Results of this work suggest that these substances are present only in minor proportions, if at all. For studies of chemical constitution of tannins most workers have purified their raw material by precipitating or extracting the tannins repeatedly with one solvent until a constant analytical figure has been attained. The results of this work show that the compounds have distribution coefficients that are close together. One would expect the solubilities to be similar also. Thus it appears unlikely that tannin components with similar properties will be separated by the solvent method. This aspect is being studied in connection with the examination of new tanning materials.

R. H. T.

**Acid and Salt Committee Report No. 1.** By R. L. Okell (Covener). *J. Soc. Leather Trades Chemists*, **35,** 225 (1951). During the life of this committee it has extended its study to include resin tube assemblies described by Cheshire, Brown and Holmes, and by Tolliday, Thompson and Forman. [See *This Journal*, **44,** 343 (1949)] and has shown that contact from 5 to 10 minutes is adequate. The later types of resin are more readily washed than the older types used in the early investigations of the committee. Extracts examined were mimosa, sulfited quebracho, chestnut, myrabolam and tannery liquors. The data obtained is shown in tabular form. The committee proposes a provisional method for determination of salts in materials, liquors and extracts by ion exchange resins and describes the method in detail.

R. H. T.

**Theories of Vegetable Tannage. A Review in the Light of Modern Theories of Colloid Science.** By A. E. Alexander, *J. Soc. Leather Trades Chemists*, **35,** 230 (1951). The author quotes Shuttleworth and Cunningham to the effect that the conception of vegetable tannage is still confused, the following theories being held: adsorption theories; coordination with peptide groups; bridge concept; electrovalent theories; polar adsorption and hydrogen bond. In view of this multiplicity of theories the trend is toward a synthesis of certain aspects culled from existent theories rather than development of new theories. Following this line the author discusses structure of initial materials (raw hide and tannin) absorption processes, penetration processes and fixation processes. For simplicity he considers raw hide as collagen and tannin as a single homogenous entity. While not true he considers that it does not modify general conclusions. Collagen is considered as a fibrous protein with ionic, ion-dipole, dipole-dipole and Van der Waal's forces operating between the polypeptide chains. At shrinkage temperature sufficient internal movement becomes possible to permit the formation of new bonds previously impossible because of steric hindrance. The importance of steric factors should be emphasized in all systems containing

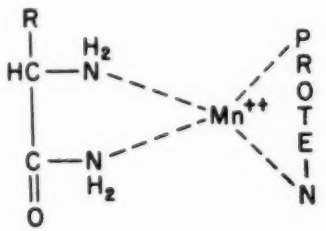
extended protein chains. The tannin is assumed to contain no groups ionized over the pH range of 3–6. The molecules will tend to aggregate because of Van der Waal's forces, i.e., resembling a typically aggregating non-ionic colloid. The first stages of absorption would involve adsorption on the outer surfaces, the thickness of the layer varying with a number of factors such as surface charge of the collagen, size of the charge of the tannin aggregates, concentration of tannin, pH, salt, non-tans, etc. From this surface layer penetration is probably an "activated diffusion" from one adsorption point to another. Owing to their higher rate of diffusion the single tan molecules are important, an increased aggregation reducing penetration through reduction of single molecules. Most tannin solutions are probably "supersaturated" which raises concentration of single molecules and increases penetration. The degree of swelling will modify micro, macro and molecular structures leading to changes in pore size and changes in the crystalline and amorphous regions. At molecular levels these changes will alter steric factors which probably often limit tanning diffusion. Factors determining swelling are well known. Fixation may take place through attachment of polar groups such as $-NH_3^+$, COOH, $>$ CO and $>$ NH, with hydroxyls and pyran oxygen; and with non-polar groups due to London (Van der Waal's) forces between tannin and protein. The importance of association through non-polar parts of the tannin molecule and the protein side chains seems to have been largely overlooked. A linkage may take place in which a tannin molecule is linked to an $-NH_3^+$ of the protein, aggregated with other tannin molecules one or more of which are hooked up again with another protein side chain, thus fastening the aggregate at both ends. Such a linkage would result in a firmly fixed tannin and a high shrinkage temperature. On the other hand, if linked at only one point, the shrinkage temperature would be but little changed and the tannin readily removed. The author concludes with four suggestions for study of aspects of the problem. They are (a) purification and separation of tannin from natural sources with the design of studying size, shape, charge, etc., of aggregates formed; (b) investigation of tanning of simpler systems both in bulk tanning and in monolayer tanning, using such synthetic tans as polyvinyl alcohol and still simpler compounds giving molecular solutions in water such as the dibasic phenols, amines, etc.; (c) quantitative study of energy of association of important groups in presence of aqueous medium; (d) tanning in presence of surface active agents. R. H. T.

**The Separation of Basic Chromium Salts By the Use of Aqueous Alcohol.** By P. S. Briggs. *J. Soc. Leather Trades Chemists*, **35**, 235 (1951). Advantage is taken of the fact that the hexa-aquo or violet form of chromium salt is insoluble in 75 per cent alcohol, at the concentrations used, while the green form, in which much of the sulfato is within the complex, remains in solution. The work deals with the solubility of basic salts in different strengths of alcohol and indicates a method by which it might ultimately be possible to learn about the composition of chrome tanning salts. If alcohol is added to basic chromium sulfate, precipitation begins when the mixture is between 30 and 40 per cent, the precipitate character depending upon basicity, concentration and previous history. As basicity of the chromium salt increases the partial solubility in aqueous alcohol decreases. As strength of solvent increases the solubility of any basic salt decreases. Roughly the solubility at 50 per cent basicity, with equal parts of industrial spirit and water, is about a quarter of the solubility at 33 per cent basicity. All existing methods of examination of basic chromium liquor give averages of the complexes. These include the Proctor-McCandlish titration, the molecular weight determined by diffusion and Shuttleworth's electrometric titration. Dialysis of fractions may make possible a determination of the proportion of the various molecular sizes, but anything which disturbs the equilibrium of the solution creates a dynamic condition. Two chrome liquors which give the same broad analytical characteristics can be very different in the actual tanning of leather. However, by disturbing the

dielectric constant of the solvent some measure of fractionation may be obtained without direct chemical interference with the complexes. This appears to be possible by the use of alcohol-water mixtures in the presence of an amount of chromium far in excess of the solvent properties of the mixture. Use of too much alcohol causes hydrolysis which increases with increase in alcohol concentration. For, as the green form of chrome alum is more soluble in alcohol-water mixtures than the violet form, and since increase in basicity brings with it a decrease in alcohol solubility, so an unstable fraction of chrome liquor in strong alcohol hydrolyses toward a more soluble acid complex, and the more basic complex, consequent on this action, comes out of solution. This fact prevents the use of increasing alcohol strengths as a method of separation of chrome liquor, though such concentrated alcohol-water mixtures may be used as a measure of the resistance of a mixed basic chrome salt to hydrolysis. Thus this weak point in the use of alcohol for fractionation may be turned to good account. Since hydrolysis does occur, it means that separations effected by this means should be carried out quickly. Usually an upper layer concentration of 50 per cent alcohol is effective, but may be more or less if not satisfactory. The solubility data show that above 55 per cent solubility diminishes rapidly and increases quickly at strengths below 50 per cent. Very stable or stabilized chrome salt solutions call for a stronger alcohol, whilst more basic solutions need a weaker. Similar considerations apply to the choice of the initial chrome concentration to be employed. It is not claimed that specific compounds exist in basic chrome salt solutions which can be separated by this method. The main objective here is to examine, in a preliminary way, the underlying ideas and see whether the results agree with what is known about basic chrome salts. One factor appears repeatedly, namely: that heating a chrome liquor and fractioning immediately on cooling increases the magnitude of the first fraction. This is consistent with the accepted view that heating does favor entry of the sulfate groups into the complex. Such entry increases the solubility in alcohol-water mixtures. It also supports the idea that the solubility product (sulfate) x (Cr. complex) has some definite bearing on the separation by this method. By examining freshly made basic chrome sulfate and following the differences occurring on ageing, the increase in stability can be demonstrated. By taking commercial liquors which had aged for months or years it was found that an inorganic liquor had over half of its complexes at about the average basicity. When this equilibrium was destroyed there was a levelling up of the molecular species over a wider range. In glucose liquor the range of basicities was less with no favored type. On boiling and evaporating, the basicity range diminished at the acid end, making more soluble complexes of higher basicity. It is noticed that the glucose liquor fractions are stable on standing in contradistinction to those from inorganically reduced liquors. R. H. T.

**Polyvinyl Alcohol as a Reagent for Tannins.** By A. T. Hough. *J. Soc. Leather Trades Chemists*, **35**, 255 (1951). In a previous paper the author showed that no reaction was given by synthetic tannins under the conditions of the following test. One ml. of a mixture of equal parts of 2 per cent solution of polyvinyl alcohol and a 2 per cent solution of anhydrous sodium sulfate to 5 ml. of the tannin solution of analytical strength. Since the experience of the author indicated that the test for synthetic tannins, published by Chen, in which the phenol-aldehyde tannins are detected by precipitation with polyvinyl alcohol, was not applicable to many tannins of this group, it seemed wise to check this scheme of analysis. A number of chemists cooperated. It was found that most phenol-formaldehyde tannins do not give a precipitate with polyvinyl alcohol and that all grades of polyvinyl alcohol gave the same results. It can be stated, therefore, that polyvinyl alcohol is quite unreliable as a test reagent for synthetic tannins. Unfortunately this invalidates the scheme of analysis put forward by Chen. R. H. T.

**Specificity and Mode of Action of Proteolytic Enzymes.** By E. M. Crook. *J. Soc. Leather Trades Chemists*, **35**, 257 (1951). Twenty years ago little was known of the action of proteolytic enzymes. The usual method of classification was largely on the site of action, i.e., on a physiological basis. A table showing such a classification, as used in 1925, is given. By 1935 chemists were able to classify on the basis of molecular size of the substrates and specificity for the end groups of the polypeptide chains. A table illustrating this is given. The work of Northrop in 1932, followed by others, making possible the preparation of pure enzymes of the pancreas and their inactive precursors (the –ogens) gave knowledge of the source, crystal form, purity and molecular weights of pepsin, trypsin, alpha-chymotrypsin, beta-chymotrypsin, gamma-chymotrypsin and carboxypeptidase. Following this, peptide synthesis (by Bergmann and Zervas) made it possible to produce peptides of known composition to serve as substrates in enzyme investigations. It was quickly shown that the usually recognized "proteinases" were capable of hydrolyzing low molecular weight synthetic substrates, provided these had certain well defined characteristics. Thus the concept shifted from the idea of the attack of the large protein molecule to a highly specific action depending on groups with well developed stereochemical requirements. The specificity requirements of proteolytic enzymes, as determined by the use of crystalline enzymes and synthetic peptides, is shown in tabular form giving the essential configurations and permissible variants. Many peptidases were shown to be metal-protein complexes, in which the metal is essential and reasonably specific, for the enzyme. A list of metal activated proteolytic enzymes and their substrates is given together with the source of the enzyme and whether an $NH_2$ or COOH group is needed for the action. The metals given are Mg, Mn, Zn and Co. One important point which has emerged is that the chief difference between a "proteinase" and a "peptidase" is that the former is able to catalyze the hydrolysis of a peptide bond remote from free alpha-amino or alpha-carboxyl group, whereas the latter requires the near proximity of either or both. The proteinase can, therefore, quickly reduce a large molecule to smaller ones: but, since the smaller ones would for the most part not have the type of link susceptible to the protease, action would stop. On the basis of this new knowledge Bergman classified the peptidases as Exopepitadases and the proteinases as Endopepitades. Bergman's classification is also given in a table showing the enzyme group, requisite group in the main chain and typical side chain specifications. One interesting point emerging is the key importance of groups other than the reactive portion of the molecule, e.g., side chai s containing the benzene ring and a polar group for the reactivity of pepsin and trypsin: and the adjacent $NH_2$ and COOH groups for the pepsidadases. Stereochemically it has been found that for hydrolysis to take place the "L" configuration is required, except in the case of bonds distant from the split, which may be of the opposite configuration. The work of Smith is described giving his conception of the form the metal complexes take in their hydrolytic splitting. The bond is "straddled" as shown in one example given here chosen from several in the text. The complex here shown is formed between L-leucine amide manganese ion and leucine amino–peptidase.



Smith concludes that the straddling of the bond by the co-ordination links with the metal is a necessary criterion for hydrolysis. He also suggests that the importance of certain side chains is due to the presence of extra binding forces between the enzymes and the terminal groups of these side chains. Chelation with a metal ion must cause considerable electronic shift, but not sufficient in itself to cause hydrolysis. Therefore, the enzyme must play the double role of increasing the weakening effect and imposing extra steric requirements upon compounds potentially capable of chelation with the metal. If this hypothesis is true, the actual hydrolysis of the peptide bond probably takes place through conventional acid-base catalysis. There is evidence that this is so. Thus we are come to as near understanding the mode of action and specificity of a proteolytic enzyme as we are to understanding any other type. R. H. T.

**The Effects of Saturated Sodium Silicofluoride Solutions on Fresh Raw Hide.** By H. R. Beakbane. *J. Soc. Leather Trades Chemists*, **35**, 276 (1951). Previous studies have demonstrated that hides treated in solutions of silicofluoride are less prone to bacterial degeneration. However, a tryout in Nigeria was not favorably accepted because of the claim that it caused hair slip. In view of the importance of the subject a study was made on the unhairing of silicofluoride treated hides and the development of bacteria therein, by means of a modified methylene blue reduction test. In all cases putrefaction was much delayed by the silicofluoride treatment. In general the longer the time of treatment the less the degree of putrefaction. For a short time of storage, even a light wash caused more hair slip than would have taken place if the hide had not been treated. For storage of over 48 hours hair slip was in general somewhat less for treated than untreated hides, although hair slippage increased with time of storage in both treated and untreated hides. Silicofluoride evidently exerts a depilitory as well as a marked bacteriostatic effect. R. H. T.

**The Determination of Sulfato Groups in Cationic Chromium Complexes By Means of Quaternary Anion Exchangers.** By K. H. Gustavson, *J. Soc. Leather Trades Chemists*, **35**, 270 (1951). Cation exchangers, in which the functional group is a sulfonate, are not satisfactory for the determination of the acidity of basic chromium sulfate, free of neutral sulfates, because the results tend to be too low. Cation exchangers with carboxyls as the functional group are even less satisfactory. In order to overcome this the logical method would be to remove the sulfate ions by means of an anion exchanger, used as the hydrochloride, provided the reaction is mainly a simple exchange of $SO_4$ for Cl. This can be accomplished with aged dilute solutions of the common type of chrome liquors. For this purpose the strongly basic quaternary groups of the new type of anion exchangers, such as Amberlite IRA–400 and Dowex 2A are required. Amberlite IRA–400 was used in the form of the hydrochloride with a basic chromium sulfate of 66 per cent acidity, free of salts, corresponding to the formula $Cr_2(OH)_2(SO_4)_2$. From this a stock solution containing one equivalent of Cr per liter was made up for experimentation. At the time of using it was more than four years old. One gram (dry basis) of the exchanger (2.0 mg. equivalent exchange capacity) was shaken for 2 hours with 5 ml. solution containing 1 mg. equivalent Cr (about 0.3 mg. equivalent $SO_4$ ions). Filtrates and washings were combined up to 100 ml. and 10 ml. aliquots taken for determination of Cr, total sulfate hydrolysable ions ($SO_4$ and Cl), and chloride. Exchange resin was used in amount of 0.5, 1, 2, 3 and 4 gr. The average acidity of the cationic sulfato chromium complexes was obtained directly from the sulfate determination and indirectly from the difference between the hydrolysable anions (titrating boiling with 0.1 *N* NaOH with phenolphthalein indicator) and determination of chloride. It was found that 0.5 gr. of resin was too little and 4 gr. too much, the latter probably being due to disturbance of ionic equilibrium. The percent of acidity of sulfato–

Cr cations found directly was 33, 33 and 32 for 1, 2 and 3 gr. of resin respectively. A series of time runs ranging from 30 minutes to 24 hours established the fact that the reaction is complete in 30 minutes. The author concludes as follows: The number of sulfate groups complexly held by chromium in cationic complexes of aged, dilute solutions of basic chromium sulfates of the general types; $Cr_2(OH)_2(SO_4)_2$ and $Cr_2(OH)_2(SO_4)_2$–$Na_2SO_4$ is directly obtained by removal of the sulfate ions from the solution by means of a quaternary anion exchanger, and examining the filtrate from the exchanger for chromium and total sulfate. Using this method under standard conditions, the removal of the sulfate ions will leave the cationic chromium complexes intact. In the above compounds, the cationic complexes contain an average of one sulfate group per 2 atoms of chromium (33 per cent acidity of the sulfato chromium complexes). The same value is found for sulfato-chromium complexes fixed by collagen, by analysis of hide powder tanned by these salts after removal of the protein-bound sulfate with pyridine. Cationic exchangers of sulfonic acid and carboxylic type used for indirect determination of the composition of cation complexes, because of displacement of the sulfato group by the functional group of the resin, give low values of the acidity of the chromium cations. The results are contrary to the assertion that the sulfato groups are displaced by the carboxyl groups of collagen during tanning.—R. H. T.

**Oil for Chamoising—A Note.** By F. Stather. *J. Soc. Leather Trades Chemists*, **35,** 280 (1951). Klenow states that in the chamoising process using unsaturated oils of a given iodine value, there is a definite relation between the acid value and tanning properties, that oils with an acid value below 10 should not be used and that oils with the higher acid and iodine values need special precaution to control the process. See abstract *This Journal*, **47,** 70 (1952). The author takes issue with these claims on the basis that studies were limited to only one type of oil with a constant iodine value and that tanning properties are based on behavior in a Mackey tester rather than on actual tanning tests and determination of the combined fat. He quotes work by others, showing that their results are not in accord with the conclusions of Klenow and maintains that it proves that Klenow's conclusions as regarding the dependence of the acid value of certain oils for chamoising is not correct. R. H. T.

**The Isolation and Determination of Fatty Spue.** By S. C. Ellis. *J. Soc. Leather Trades Chemists*, **35,** 282 (1951). It has been known that fatty spue is frequently composed of high melting point fatty acids such as palmitic and stearic, and also of true triglyceride fats. Since the amount of spue, in actual weight, is so small, deducing the cause of spue has been done from total grease analyses. In this paper methods are described for the qualitative and quantitative determination of spue using a surface film balance and micro-titration. The former allows the determination of chain-length and the latter, differentiation between free fatty acid and triglycerides. Two methods were used satisfactorily for isolation of the spue. In one the spue was scraped off with a razor blade and extracted with grease-free petroleum ether in a micro-Soxhlet extractor. In the other the spue was swabbed off with degreased cotton wool soaked in petroleum ether and the swab extracted as in the other method. Determination of the hydrocarbon chain length was made by taking force-area measurements of surface films spread on 0.1*N* HCl and plotting area/molecule, $m^2$/mg against surface pressure, dyness cm. Results were compared with curves of known palmitic acid and tripalmitin as well as stearic acid and tristearin. One spue sample tested fell between the two, indicating a hydrocarbon chain length corresponding to a molecular weight of about 263 for the fatty acids and 827 for the triglycerides. Microtitration, for which the method is described, showed 21 per cent fatty acid. Therefore, the sample contains a mixture of fatty acids and triglycerides in the ratio of 1:4 respectively and chain

length of 16 to 17 total carbon atoms. Since most fatty spues are between 16 and 18 carbon atom molecules it is simpler to determine the free fatty acid as stearic acid, thereby avoiding the surface film determinations for molecular size. A second spue sample so analyzed showed 98 per cent stearic acid. Hence it was assumed that this particular spue was almost entirely fatty acid of chain length of about 18 carbon atoms. R. H. T.

**A Colorimetric Analytical Method for Pyrocatechol Tannins.** By Hans Batzer. *Das Leder*, **2**, 169 (1951). A colorimetric method for determining tannin has been described by Vorsatz [*Colloquim*, 1942, 424]. The same method was investigated by Adams and Merrill [J.A.L.C.A., **44**, 636]. The present work was undertaken to study the mechanism of the reaction. Catechol and some of its important derivatives are nitrated by nitrous acid to mono-nitro-derivatives which, on neutralization, form deep red "nitronic" acid salt solutions. The mono-derivative is destroyed by an excess of nitrous acid. The reaction is a time reaction so that an excess of nitrous acid is needed to produce the color in a short time. The time is too long (10-15 minutes) if the concentration ratio of catechol to nitrous acid is 1:5 or less. The best ratio was 1:10 for a reaction time of 3 minutes at 20°C. The neutralized solution is sensitive to oxidation by atmospheric oxygen.

The following modified method is given: Required solutions: (1) 0.25 normal sodium nitrite solution (17.25 grams $NaNO_2$ per liter), (2) 1.66 normal acetic acid solution (10 per cent solution), and (3) 2 normal sodium hydroxide solutions. The tannin solution should contain approximately 8 grams of tannin per liter. Pipette 10 cc. of the tannin solution, 10 cc. of acetic acid solution, then 10 cc. of the sodium nitrite solution into a 250 cc. graduated flask. Exactly 3 minutes after adding the sodium nitrite solution add 15 cc. of the sodium hydroxide solution, mix, and make to volume with water. After a time, which may be chosen by the operator to suit his convenience but then must not vary, the solutions are measured in a colorimeter. A catechol type tanning material carefully standardized by the International Official method may be used as a standard. A 0.025 molar catechol solution may be used as standard if the catechol radical content of the unknown is known. I. D. C.

**Observations on Box Calf Operations Between Drying and Finishing.** By F. Henacker. *Das Leder*, **2**, 172 (1951). After drying, box calf leather should be stored in a room having a relative humidity of between 80 and 90 per cent until ready for finishing. Sammying may be done either by burying in beech chips having a moisture content of 30-36 per cent, depending on the absorptivity of the leather, or by dipping mechanically for three to ten minutes in water at 40-60°C. Drying of the tacked or toggled leather should start at 25° with an increase in temperature to 35-40° in 4-8 hours. Strong air circulation during drying is not good. I. D. C.

**Chamois Tanning. I. Investigation of the Usefulness of the Mackey Test for Evaluating Tanning Oils.** By A. Kuntzel, H. Erdmann and Th. Nungesser. *Das Leder*, **2**, 196 (1951). The Mackey Apparatus [*Jour. Soc. Chem. Ind.* **15**, 90 (1896)] consists of a perforated extraction thimble of metal in an air chamber provided with chimneys for air circulation. The chamber is surrounded by a water bath in which water is kept boiling during a test. The oil to be tested is worked into a wad of cotton, the wad is placed in the thimble, the bulb of a thermometer is inserted in the wad, after which temperature readings are taken at regular intervals. By plotting temperature as a function of time, a curve is obtained which shows (a) oxidation capacity (maximum temperature) and (b) oxidation sensitivity (time to the beginning of autooxidation). The addition of paraffin oil to cod oil

lowered oxidation capacity until with 75 per cent paraffin oil there was almost no temperature rise, although sensitivity did not change. The addition of free fatty acid to soya oil did not alter capacity, but did lower sensitivity so that autooxidation started in 40-50 minutes instead of 120-140 minutes. The following relations were found between the Mackey test and the oil constants: (1) The higher the iodine number of the oil the greater its oxidation capacity, (2) the greater the acid number, the greater the oxidation capacity, and (3) the saponification number has only limited value for assessing the oxidation value of an oil. Oxidation inhibitors decreased sensitivity but did not change capacity. Iron, cobalt and copper oleates increased rate of autooxidation—copper oleate most. Nickel oleate had almost no effect. Elemental metals also speeded oxidation provided soaps were formed. After a test all of the oxidized fish oil could be extracted from the cotton with alcohol unless iron oleate was present, in which case only 70 per cent could be extracted. This indicates that iron causes a side polymerization reaction. The Mackey test permits a better characterization of the tanning behavior of an oil than the analytical values used previously. I. D. C.

**Chamois Tanning. II. Formation of Acrolein During Oxidation of Chamois Tanners' Fish Oil.** By A. Küntzel and Th. Nungesser. *Das Leder*, **2**, 233 (1951). During the oxidation stage of chamois tanning there is an unmistakable odor of acrolein. This fact indicates an aldehyde tannage, however no direct proof can be found in the literature that acrolein can be formed from fatty acids of fish oils. Salway in 1919 found that acrolein was formed on autooxidation of linseed oil and linolenic acid. The present work was a quantitative investigation of the formation of acrolein by autooxidation of fish oils.

The Mackey apparatus (see preceding abstract) was modified so that a preheated mixture of two parts nitrogen and one part oxygen could be supplied to the oxidation chamber. The gas from the chamber passed through two gas washing bottles and the wash water was tested for acrolein. Positive results were obtained with all of the numerous tests tried. For example, bromine was decolorized, permanganate or ammoniacal silver nitrate solutions were reduced, a gentian blue color was formed with piperidine and sodium nitroprusside, a helio red color with phenol, sulfuric acid and 95 per cent alcohol, and a blue color with phloroglucin. A hydrazone of proper color was obtained with p-nitrophenylhydrazine. A quantitative determination of acrolein was made by using a 2 normal hydrochloric acid solution of p-nitrophenylhydrazine in the wash bottles then filtering off and weighing the hydrazone. At the temperature of boiling water brown cod oil produced 1.21 per cent and light cod oil 0.74 per cent acrolein (on the oil basis) while at the temperature of boiling alcohol (78°C.) the corresponding values were 1.16 per cent and 0.74 per cent respectively. As the bath temperature (in the Mackey tester) influences the height of temperature rise in the Mackey test, the acrolein method is better than the Mackey test for testing the quality of an oil.

The obvious source of acrolein would be the glycerin, but glycerin in the Mackey tester produced no acrolein. From a mixture of cod oil and glycerin, less acrolein was formed than from the oil alone, and purified fatty acids yielded more acrolein than the oil from which they were derived. Acrolein therefore is formed from the fatty acid.

When pure nitrogen was passed through the Mackey tester, some acrolein formed at first because peroxides formed during loading of the tester (saturating the cotton with the oil, etc.). After peroxides were removed no more acrolein formed unless oxygen was added to the gas stream. A mixture of hide power and oil in the Mackey tester at 78°C. gave off only a little acrolein showing that it was fixed in the nascent state by the hide powder. I. D. H.

**A Semimicro-Determination of Tannin by the Filter Method.** By W. Grassmann, O. Endisch and W. Kuntara. *Das Leder*, **2**, 202 (1951). Many simple or rapid methods have been proposed for determining tannin, however, all oxidimetric, iodimetric, nephelometric, colorimetric or precipitation methods have the fault that standard curves are required for each tanning material. The results are questionable and often useless with mixtures or with unknown substances. The following semimicro method has proved satisfactory in many hundreds of determinations. The samples were ground in a "chewing machine for stomach patients". Use a one gram sample for moisture. Leach in a Koch extractor 2.5 cm. in diameter and 6 cm. high. Use one-tenth the normal amount of sample and collect 50 ml. of extract at 50°C. in 3 hours, then 50 ml. at 100° for a total of 100 ml. in 6 hours. Determine total solids by drying 5 ml. at 100° to constant weight in a small silver dish (3 × 2 cm.); 4-6 hours will be required. For soluble solids the solution is filtered through a candle 60 mm. long and 15 mm. in diameter; discard 25 ml. then collect and evaporate 5 ml. Detannize by the Procter method, using a filter bell 50 mm. long and 11 mm. in diameter with a capillary tube 1.5 mm. in diameter and 320 mm. long. Use 0.7 grams of fine, weakly chromed hide powder, packed into the tube so it will not fall out. Discard 3 ml. of the filtrate, then collect 6 ml. and evaporate and weigh 5 ml. Results by this method agree well with those by the usual macro method. On 49 samples (10 materials) the ratio of tannin by the micro method to that by the macro method varied from .93 to 1.035 with an average of .9986. I. D. C.

**Pliability in the Dressing of Fur Skins.** By H. Erdmann and U. H. Dienstmann. *Das Leder*, **2**, 173 (1951). To obtain pliability, a long liming, strong bating and an empty tannage are necessary. The mobility of the skin network is decreased by either slack tannage, so that the skin fibers are glued together or by the excess tannin in overtannage. Muscular tissue must be removed or the skin will not be pliable. This tissue is easily removed from some skins, but from others (e.g., rabbit) it must be shaved off. Soak waters containing salt or formic acid, extracted 30-40 per cent more collagen than water soaks, but after formaldehyde tannage of these skins, pliability was best for skins soaked with salt and poor for skins soaked with addition of formic acid. Intensifying the action of the soak liquor is not sufficient to give satisfactory pliability. There was direct relation between sulfuric acid concentration of the pickle, loss of protein from the skin and pliability. Chrome and formaldehyde tanned pelts required an acid pickle, but pliable alum tanned pelts could be obtained under certain conditions without a sulfuric acid pickle. Formic acid was not as good as sulfuric for the pickle. Pliability, both perpendicular and parallel to the backbone line, was measured with a machine by means of which a required load could be easily applied and removed from a specimen. Stretch under load and then after removal of the load was measured at increasing loads (increments of 1 kilogram per unit area) from one kg. to breaking load. Pliable fur leather has nearly the same stretch in the parallel and perpendicular direction. I. D. C.

**Tanniferous Kinds of Polygonum.** By St. Hemberg. *Das Leder*, **2**, 239 (1951). Two rank growing species of *Polygonum* were considered in 1942-3 as sources of tannin to relieve the shortage in Sweden. *Polygonum sachalinense* reaches a height of almost 3 meters, and the leaves, which often reach a size of 35 × 25 cm., contain 20-30 per cent of tannin. A sample collected in September contained 24.3 per cent tannin in the leaves and 5.9 per cent in the stems; the corresponding purities were 66 and 38. *Polygonum cuspidatum* reaches a height of 2.5 meters. A typical sample contained 17.4 per cent tannin in the

leaves, 13.4 per cent in the twigs and 3.3 per cent in the stems with corresponding purities of 59, 51 and 26. The plants are leafy, rapid growing and thrive on poor soil. On marshy ground they make vigorous growth, but the tannin content and purity are low. The following extraction procedure was suitable: Soak 24 hours in 10 volumes of water, boil under reflux for 5 hours, then extract at 100°C. to 2 liters in 5 hours. The tannin is of the pyrocatechol class. The tannin content was highest in summer and in fall, so that there is a long harvest period. The yield of tannin was increased from 16.5 per cent (purity 60.4) to 26.2 (purity 66.3) by extraction with 2.7 per cent sodium sulfite or to 29.1 per cent (purity 73) by extraction with 3.5 per cent sulfite. Calf leather tanned with extract was good, except in pliability. It was rather dark, but bleached to a very light color. The extract made good, firm sole leather, with a mangrove-like color. The leather yield was 56-58 per cent. I. D. C.

**Some Austrian Auxiliary Materials.** By Erich Schmid. *Oesterreichische Leder-Zeitung*, **6**, 275 (1951). Brief description of some products, both old and new, used in the beam house and for tanning and finishing. I. D. C.

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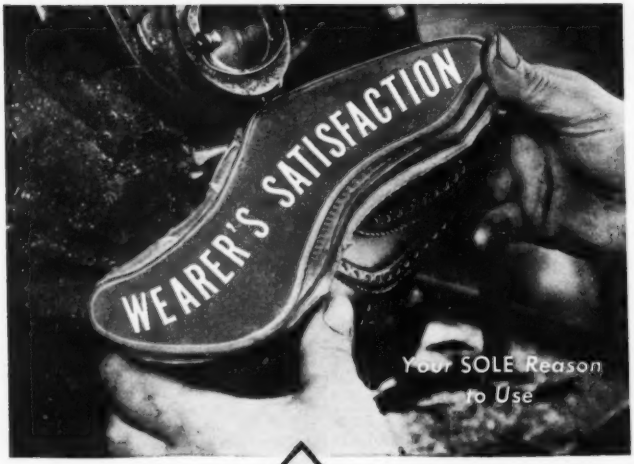


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# CHESTNUT

## ITALIAN EXTRACT

highest quality — made under
the supervision of the world's
leading extract chemists

**Cipec Brand**

**TYPICAL A.L.C.A. ANALYSIS**

| | Solid | Powder | Spray Dried |
|---|---|---|---|
| TANNIN | 61.72 | 66.7 | 73.5 |
| NON-TANNIN | 21.65 | 21.2 | 19.1 |
| INSOLUBLES | .65 | .6 | .7 |
| WATER | 15.98 | 11.5 | 6.7 |
| ASH | .67 | .82 | .75 |

Clean Light Color — Smooth Silky Grain

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SOLE AGENTS
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# MYRTAN

## A TANNING EXTRACT

made from the wood of an Australian species of the Eucalyptus family. It contains both catechol and pyrogallol tannin, the latter predominating.

**TYPICAL A.L.C.A. ANALYSIS**

| | |
|---|---|
| TANNIN | 61.55 |
| NON-TANNIN | 16.03 |
| INSOLUBLES | 1.70 |
| WATER | 20.72 |

Also Available as Liquid with 30% Tannin

As a retanning agent for chrome tanned leather, Myrtan possesses many advantages, such as smooth and strong grain, good color and break, as well as a round feel.

Blended into sole leather tannages, it has given better yields and improved color.

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